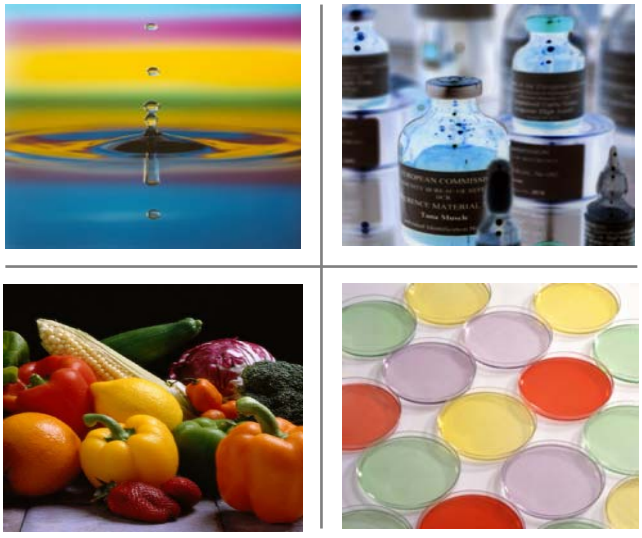
EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

The Certification of the Mass Fractions of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, V and Zn in fly ash BCR-176R

A. Held, G. N. Kramer, P. Robouch, U. Wätjen



Report EUR 22667 EN

The mission of IRMM is to promote a common and reliable European measurement system in support of EU policies.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
A. Held
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

E-mail: andrea.held@ec.europa.eu

Tel.: +32 (0)14 571 957
Fax: +32 (0)14 571 548

http://www.irmm.jrc.be
http://www.jrc.ec.europa.eu

EUR Report 22667 EN
ISBN 978-92-79-04998-9
ISSN 1018-5593
Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Reference Materials and Measurements

The Certification of the Mass Fractions of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, V and Zn in fly ash BCR-176R

A. Held, G. N. Kramer, P. Robouch, U. Wätjen

Summary

This report describes the preparation and certification of the fly ash Certified Reference Material (CRM) BCR-176R. It replaces its exhausted predecessor, BCR-176. The CRM was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRM was prepared from a fly ash collected in the electrostatic filters of a city waste incineration plant. After milling the resulting powder was filled in glass bottles containing 40 g powder.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The new CRM has been certified for its content of As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Se, Tl and Zn .

Indicative values have been established for Hg, Mn and V.

This CRM is intended for use in quality assurance of measurements of heavy metals in fly ash and related matrices

	Mass Fraction	
	Certified value [1] [mg / kg]	Uncertainty [2] [mg / kg]
As	54	5
Cd	226	19
Co	26.7	1.6
Cr	810	70
Cu	1050	70
Fe	13100	500
Ni	117	6
Pb	5000	500
Sb	850	50
Se	18.3	1.9
Tl	1.32	0.21
Zn	16800	400

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.

2) Expanded uncertainty with a coverage factor k = 2 according to the Guide for the Expression of Uncertainty in Measurement, corresponding to a level of confidence of about 95 %.

Table of contents

Glossary

AAS	atomic absorption spectrometry
AFS	atomic fluorescence spectrometry
ANOVA	analysis of variance between groups
CRM	certified reference material
CVAAS	cold vapour AAS
CVAFS	cold vapour AFS
ETAAS	electrothermal AAS
ET	electrothermal evaporation
FAAS	flame AAS
HG	hydride generation
ICP-OES	inductively coupled plasma optical emission spectrometry
ICP-MS (Q / HR / MC)	inductively coupled plasma mass spectrometry (quadrupole / high resolution i.e. sector field / multicollector instrument)
ID	isotope dilution technique
ID-TIMS	thermal ionization mass spectrometry using the isotope dilution technique
INAA	instrumental NAA
k	coverage factor
k_0-NAA	NAA using the k_0-method for quantification
M	minimum sample mass
MS_{among}	mean square among bottles from an ANOVA
MS_{within}	mean square within a bottle from an ANOVA
NAA	neutron activation analysis
RSD	relative standard deviation
RNAA	radiochemical NAA
rel	Relative (as subscript)
s_{bb}	between-unit variability
s_m	relative standard deviation of the homogeneity experiment
s_{meas}	measurement variability
s_{method}	method variability
SI	Système International d'unités (international system of units)
u_{bb}	uncertainty related to a possible between-bottle inhomogeneity
u_{bb}*	uncertainty related to inhomogeneity that could be hidden by method repeatability
u_c	combined uncertainty of the certified value
$u_{c,bb}$	combined uncertainty of the between-unit measurement
u_{char}	uncertainty of the characterisation
U_{CRM}	expanded uncertainty of a certified value
$u_{dry\ mass}$	uncertainty contribution covering variations in dry mass
U_{ind}	expanded uncertainty of an indicative value

u_{lts}	uncertainty of stability
u_R	relative uncertainty of reproducibility
u_{st}	relative uncertainty of the calibration standard
u_{target}	maximum relative uncertainty for sampling
ZAAS	AAS using a Zeeman background correction

1. Introduction

This report describes the preparation and certification of a fly ash reference material, BCR-176R. It replaces the exhausted BCR-176.

Incineration of waste produces a range of potentially harmful residues, air emissions, water discharges and residues like ashes and slags. The solid residues may be processed further for use in concrete or road construction, if they do not release toxic elements into the environment. Analysis of fly ash is therefore necessary. Directive 2000/76/EC [1] on the incineration of waste also requires measurements of heavy metals in air emissions and water discharges, also here a large fraction of the heavy metals are present as particulate matter and will require similar analytical methods as for fly ash. Certified Reference Materials (CRMs) are an essential tool in establishing comparability, and this particular CRM may be used for quality assurance of measurements of heavy metals in fly ash and related matrices.

Certified values for the mass fractions of As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Se, Tl and Zn in this material were established, as well as indicative values for Hg, Mn and V.

2. Participants

Participant	Activity[1)]
Free University of Amsterdam, Institute for Environmental Studies (IVM), Amsterdam, NL	P
Municipal Incineration Plant (AVI), Amsterdam, NL	P
European Commission, DG JRC, Institute for Reference Materials and Measurements (EC-JRC-IRMM), Geel, BE	P, H, S, C
Water Research Centre (WRc-NSF Ltd), Analysis Department, Medmenham, GB	H, S, C
Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, DE	C
Centre National de la Recherche Scientifique (CNRS), Service Central d'Analyse, Vernaison, FR	C
Laboratoire National d'Essais (LNE), Paris, FR	C
Nederlands Meetinstituut (NMi) - Van Swinden Laboratorium, Delft, NL	C
Nuclear Research and consultancy Group (NRG) Petten, Isotope Specific Analysis, Petten, NL	C
Risø National Laboratory, Risø, DK	C
Siemens AG, Energieerzeugung (KWU), Erlangen, DE	C
University of Pavia, Nuclear Chemistry, Pavia, IT	C
University of Gent, Institute of Nuclear Science (INW), Gent, BE	C
Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE	C

[1)] P: production of the material, H: homogeneity study, S: stability study, C: characterisation study

3. Processing of the materials

This material is a fly ash collected in the electrostatic filters of an incineration plant for city waste. The fly ash was sampled by Dr. F. Ariese of the Institute for Environmental Studies (IVM) of the Free University of Amsterdam at the municipal waste incineration plant (AVI) of Amsterdam. The municipal waste consists of about 60 % domestic waste and 40 % inflammable, non-chemical waste from small commercial companies. The waste was burnt without prior sorting treatment and no combustion additives were applied. The temperature in the furnace was about 900 – 1000 °C. The plant operates four furnaces with a total emission of 500 000 $m^3 \cdot h^{-1}$ exhaust gases with a solid content of 2 $g \cdot m^{-3}$.
The batch of 1000 kg, packed in two large bags, was collected from the electrostatic filters of one furnace over a period of 4 h and dispatched to IRMM for further treatment [2]. The water content of the starting material corresponded to less than 1 % (mass fraction).

Fine grinding of the incineration ash was carried out using a jet mill and ultrafine classification system. In the jet mill, three nozzles are mounted at the bottom of the grinding chamber to blow air jets of 6 bar. The three-dimensional nozzle arrangement enables the feed material to be completely ground without residue. The air jets accelerate the feed particles to impact on each other, thus reducing in size through wear from identical material without any contamination from foreign grinder material. Furthermore, all surfaces of the milling and sorting system, which come into contact with the products, are made of aluminium oxide ceramics, polypropylene or polyurethane in order to minimize contamination risks. Fine particles are extracted through the classifying wheel. They can be extracted into a sharp size distribution within a range between 5 and 120 µm depending on the feed material and operating parameters. Coarse particles flow back along the wall into the grinding chamber and are re-injected in the grinding process.
The grinding process was performed with a speed of the classifying wheel of 7000 rotations per minute. A total amount of 195 kg ground incineration ash powder with a top particle size < 105 µm was produced with a mean production rate of 2.2 $kg \cdot h^{-1}$.

Homogenisation and bottling were carried out in a multi-purpose cone mixer of 250 L volume with semi-automatic filling equipment.

After jet milling the material was directly introduced into the cone mixer by a central filling nozzle on top of the mixer. All drives and gears are placed outside the mixing chamber in order to exclude contamination by oil. All parts of the mixer in contact with the powder are made of polished stainless steel. A potential contamination from the processing equipment would not have an impact on the quality of the final CRM as certification is done after processing and bottling.

A feed screw at 100 mm from the bottom of the mixer allows filling of vials without stopping mixing with a given mass of material. Directly after filling of a bottle, the feeder turns into the opposite direction to push the powder back into the cone mixer.

A mean production rate of 100 bottles per hour was achieved. A total number of 4345 bottles were filled with 40 g powder in 100 mL amber glass bottles, which were closed with an insert of polyethylene and a screw cap.

Particle size measurements were carried out using a Sympatec particle size analyser with a HELOS measuring device. A representative example of the particle size distribution is given in Figure 1, indicating a peak particle size of 20 µm and a particle size < 105 µm.

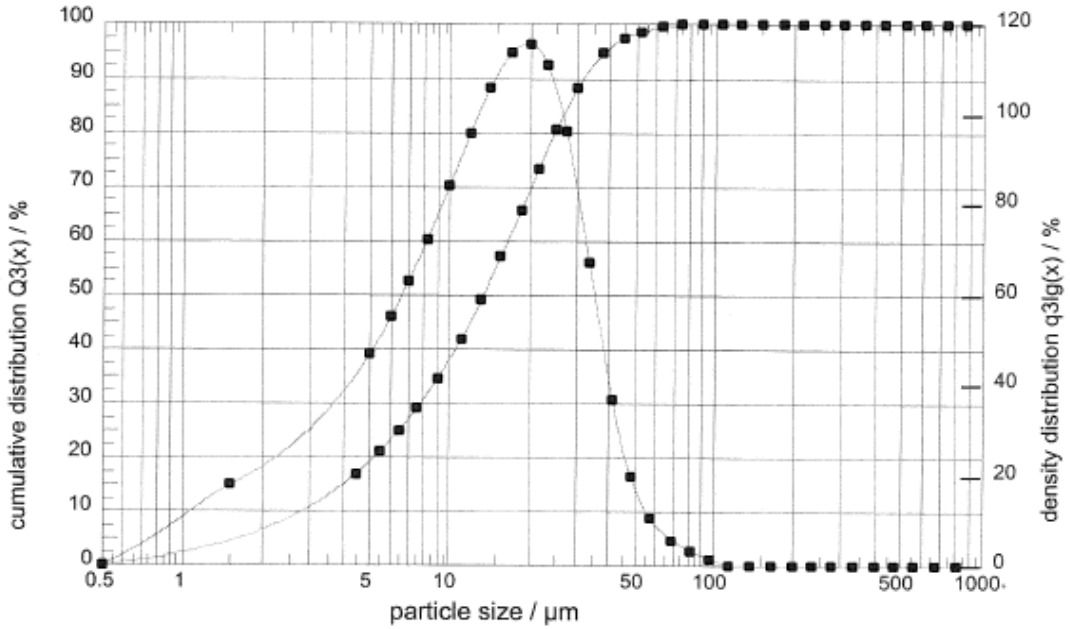


Figure 1: Particle size distribution of the BCR-176R fly ash

Representative samples were taken to determine the water content of the processed powder with a Karl Fischer method. The results of the water determinations directly after bottling were:

$\bar{x}$ = 1.24 %, *s* = 0.10 %, *n* = 20

4. Homogeneity

4.1. Between bottle homogeneity

The between bottle homogeneity is tested to ensure that the certified values of the CRM are valid for each individual bottle of the material, within the stated uncertainty. For homogeneity testing of the materials, 20 bottles were selected at regular intervals throughout the produced batch. For assessment of homogeneity one subsample of each of the (k = 20) bottles was analysed. To assess the method variability (n = 6) subsamples of one bottle were analysed.

The results of these measurements were evaluated using a method described by Linsinger *et al*. [3].

The obtained data are first tested if they follow a normal, or at least unimodal distribution. This is done by visual inspection of normal probability plots and histograms. If the data does not follow at least a unimodal distribution, the calculation of standard deviations is doubtful or impossible. Next, the method variability s_{method} is defined as the standard deviation of the n = 6 results of one bottle. The combined uncertainty of the between-bottle measurement $u_{c,bb}$ is defined as the standard deviation of the results of the 20 different bottles. The variation of the measurement s_{meas} is equal to s_{method}, as only one sub-sample per bottle has been measured. u_{bb}* is the inhomogeneity that could be hidden by the method repeatability.

$$u_{bb}^{*} = s_{meas} \sqrt[4]{\frac{2}{n-1}}$$

The variation between bottles s_{bb} is calculated as $\sqrt{u_{c,bb}^2 - s_{meas}^2}$ if the argument under the root is valid. The uncertainty related to a possible between-bottle variation u_{bb} is then the larger of u_{bb}* and s_{bb}.

The elements As, Cd, Co, Cr, Fe, Sb, Se and Zn have been measured by k_0-NAA, the elements Cd, Cu, Hg, Mn, Ni, Pb, Se, Tl, V, Zn by ICP-MS, Hg by CVAAS and Se by HGAAS (see Annex 2). Unfortunately, the lab using ICP-MS, CVAAS and HGAAS used an aqua regia leach only for the measurements. If the aqua regia leachable part of the different elements is distributed homogeneously, it is assumed that this would also be valid for the total content. Therefore these results will be used to assess homogeneity, but only for those elements where no k_0-NAA data is available (Cu, Hg, Mn, Ni. Pb, Tl, V). The aqua regia leachable mass fraction is somewhat lower than the total contents (see Table 1).

Table 1: Comparison of aqua regia leachable content and total content

Element	Cu	Hg	Mn	Ni	Pb	Tl	V
Mean value from homogeneity study (aqua regia leach) [mg/kg]	952	1.4	680	100	4600	1.0	30
Mean value from characterisation (total content) [mg/kg]	1050	1.6	730	117	5000	1.3	35

In order to calculate the above mentioned standard deviations, such as s_{method} and $u_{c,bb}$, the data should follow a normal or at least unimodal distribution. This was tested using a visual evaluation of normal probability plots plotted from the data available. Results are summarised in Table 2.

Table 2: Summarised results of the test of the distributions of the data for the homogeneity study (* data follows neither a normal nor a unimodal distribution)

Element	Distribution of data from homogeneity study	Distribution of data from stability study	Distribution of data from characterisation study
As	Unimodal		
Cd	Unimodal		
Cr	Normal		
Co	Unimodal		
Cu	None*	None*	Normal
Fe	Unimodal		
Hg	Unimodal		
Mn	None*	None*	Unimodal
Ni	None*	Normal	
Pb	Unimodal		
Sb	Normal		
Se	None*	Normal	
Tl	None*	None*	Unimodal
V	Unimodal		
Zn	None*	Normal	

For most elements (As, Cd, Cr, Co, Fe, Hg, Pb, Sb and V) the data follow a normal or at least unimodal distribution. For some elements this is not the case. Here other available data were used to evaluate homogeneity of the material. First, data from the stability study were scrutinised for applicability. In case no significant instability is detected (as found here) stability data can also be used to assess homogeneity. For the elements Mo. Se and Zn the stability data follow a normal distribution and were used to evaluate homogeneity. For Mn, Tl and Cu this was not the case. For these elements, data from the characterisation study were evaluated using 2 way ANOVA to obtain an estimate for u_{bb}. The resulting data for u_{bb} are summarised in Table 3.
The consistency of the resulting data confirms that the homogeneity of the material is under control, and points towards the fact that the non-normal and non-unimodal distribution of the data for some elements from the homogeneity or stability study is merely a measurement artefact and not due to a problem with the material homogeneity.

Table 3: Data for the uncertainty on the homogeneity u_{bb}

Element	u_{bb} (%)	u_{bb}* (%)	s_{bb} (%)
As	1.59	1.59	1.51
Cd	3.56	2.98	3.56
Cr	0.93	0.93	---
Co	0.86	0.86	0.3
Cu	2.30	0.62	2.30
Fe	0.74	0.75	0.67
Hg	4.04	1.77	4.04
Mn	1.65	0.93	1.65
Ni	1.50	0.43	1.50
Pb	4.10	1.56	4.10
Sb	0.50	0.50	0.23
Se	2.01	2.01	---
Tl	3.69	0.60	3.69
V	4.37	2.07	4.37
Zn	0.41	0.41	---

4.2. Minimum sample intake and micro-homogeneity

The minimum sample intake is the smallest sample mass for which the certified values and their uncertainties are still valid. At least this mass should be used in the analysis of the CRM. When smaller sample sizes are used, the uncertainties of the certified values should be increased accordingly.

The micro-homogeneity of the materials was assessed using electrothermal evaporation (ET) ICP-MS [4] for elements under investigation except V. Sample intakes of about 0.8 mg were used. 75 - 85 replicate measurements were carried out per element except Tl (42 replicates) on samples taken from 9 (Tl: 5) different bottles [5].

The data has been evaluated according to the following equation [6]:

$$M = \left(\frac{k_2' \cdot s_m}{u_{target}} \right)^2 \cdot m$$

where M is the minimum sample mass, k'_2 factor for the two-sided 95 % tolerance limits for a normal distribution, s_m relative standard deviation of the homogeneity experiment, u_{target} maximum relative uncertainty for sampling and m average mass used during the measurements.

In this case, the square root of MS_{within} from an ANOVA of the microhomogeneity data is used for s_m, i.e. only the within bottle variance is considered for the microhomogeneity.

The resulting minimum sample masses are summarised in Table 4.

Table 4: Minimum sample masses M for a target uncertainty of 5 % as determined by ET ICP-MS

Analyte	M [mg]	s_m [%]	m [mg]
As	11.9	8.5	0.806
Cd	18.2	10.5	0.806
Co	54.0	18.1	0.806
Cr	19.9	11.0	0.806
Cu	4.0	4.9	0.806
Fe	39.1	15.4	0.806
Hg	20.2	11.0	0.808
Mn	15.2	9.6	0.801
Ni	47.6	17.0	0.806
Pb	10.3	7.9	0.806
Sb	28.9	13.2	0.803
Se	15.2	9.6	0.806
Tl	28.4	12.2	0.798
Zn	5.9	6.0	0.797

All results for the minimum sample intake are below 50 mg with the exception of Co (54 mg). No data is available for V, but it is assumed that it should not differ significantly from the other elements. Anyhow, for V only an indicative value will be given (see chapter 7). Therefore the overall minimum sample intake for the material can be set to 50 mg.

5. Stability

The stability study combines both long-term stability and short-term stability.

The long-term stability is tested to establish the shelf life of the CRM. The CRM is tested over a certain period of time, from which a prediction for the future is calculated. The short-term stability is tested to establish dispatch conditions for the material. During transport, especially in summer time, quite high temperatures can be reached. This is simulated in the short-term stability study. In case of the fly ash material, these two studies have been combined.

The stability of the fly ash has been tested over a period of 2 years using an isochronous storage design with time points at 0, 6, 12, 18 and 24 months [7]. Storage at 18 and 40 °C has been tested, covering both long-term and short-term stability, respectively. A temperature of -20 °C has been used as reference temperature for the isochronous storage design. Additional stability measurements were carried out at a later stage, providing an additional time point at 88 months, 18 °C for all elements except Cr.

The elements As, Cd, Co, Cr, Fe, Sb, Se and Zn have been measured by k_0-NAA, the elements Cd, Cu, Hg, Mn, Ni, Pb, Se, Tl, V, Zn by ICP-MS, Hg by CVAAS and Se by HGAAS (Lab 07, see Annex 1). Unfortunately, the lab using ICP-MS, CVAAS and HGAAS used an aqua regia leach only for the measurements. Any degradation of the matrix of the material should result in a change of the leachability of the analytes. If the aqua regia leachable part of the different elements is stable, it is assumed that this would also be valid for the total content. Therefore these results will be used to assess stability, but only for those elements where no k_0-NAA data is available (Cu, Hg, Mn, Ni. Pb, Tl, V). The aqua regia leachable mass fraction is somewhat lower than the total contents (see Table 1 in the previous section).

The additional data obtained for the 88 months time point are based on a complete digestion of the samples and not on an aqua regia leach as the earlier data. To allow a combined evaluation of all data, the data sets were normalised to their respective averages.

All data used for the evaluation of stability are summarised in Annex 3.

The data points were plotted against time and the regression line was calculated. In all cases the slope of the regression line was found to be insignificant. The uncertainty of stability u_{lts} of the materials is then calculated for the required shelf life as:

$$u_{lts} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot x$$

where *RSD* is the relative standard deviation of all results of the stability study, x_i is the time point for each replicate, $\bar{x}$ is the average of all time points and *x* is the proposed shelf life (120 months in this case).

The results are summarised in Table 5.

Table 5: Relative uncertainty of the stability u_{lts} for a shelf life of 120 months

element	18°C u_{lts} (%)	18°C Slope significantly different from 0 at 99 % and 95 % confidence	40°C Slope significantly different from 0 at 99 % and 95 % confidence
As	2.2	No	No
Cd	1.2	No	No
Cr	3.3	No	No
Co	1.1	No	No
Cu	1.2	No	No
Fe	0.9	No	No
Hg	1.7	No	No
Mn	1.8	No	No
Ni	1.3	No	No
Pb	1.5	No	No
Sb	0.9	No (at 99 % confidence), Yes (at 95 %)	No
Se	3.8	No	No
Tl	6.0	No	No
V	4.0	No	No
Zn	0.7	No	No

Within the stated uncertainties the material is expected to be stable for 120 months when stored at 18 °C. Also the former BCR-176 was stored at 18 °C and did not show any instability over 10 years. Nevertheless, the material will be subjected to IRMM's regular stability monitoring programme to ensure stability.

6. Characterisation

6.1. Methods used

The methods used in the characterisation study are summarised in Annex 1. The participants received two bottles of each material and were requested to provide 6 independent results, 3 of each bottle. In addition, the water content had to be determined on separate test portions.

As a quality control measure, the participants also received a bottle of BCR-176. Two replicate results had to be provided for this sample. The results for this sample are not reported here but have been used to support the evaluation of results to identify outliers.

Individual results of the participants, grouped per element and material are displayed in Annex 4.

6.2. Dry mass correction

No fixed protocol was given to the participants of the characterisation. This resulted in a variety of drying methods applied in the characterisation, which are listed in Table 6.

Table 6: Drying methods and reported results as applied in the characterisation study

Lab code	Sample mass [g]	Drying temperature [°C]	Time [h]	Reported mass loss [%]	
01	2.5	110	4	0.35	0.46
02	1	103	17	0.19	0.182
03	9	105	14	< 0.05	
04	1.5 -2	105	Not reported	< 0.01	
05	18 – 1.9	102	> 2 – 3	< 0.1	0.11
06	2.8 3.5	105	2	1.27	1.32
07	5	105	Not reported	0	
08	1.1 1.3	103	3	1.209	1.211
09	2	Not reported	2	1.16	1.10
10	1.3	Room temperature, over P_2O_5	1 month	Increase by 0.064	0.080
11	1	107	> 24	0.33	0.20
12	1.2 - 2	Karl-Fischer titration after equilibration in a 50 % humidity atmosphere		1.55	2.02
				1.72	1.66

Additionally the water content of the material was determined by Karl-Fischer titration directly after filling it into the bottles. This resulted in a water content of 1.24 ± 0.02 % (mass fraction, uncertainty is one standard deviation based on n=20 determinations). Measurements of the water activity and of sorption isotherms on this material also indicate that the material is strongly hygroscopic (Figure 2). Investigations have shown that the increase in mass shown in the Figure is reached already after short exposure (10 min) to an atmosphere with a given relative humidity.

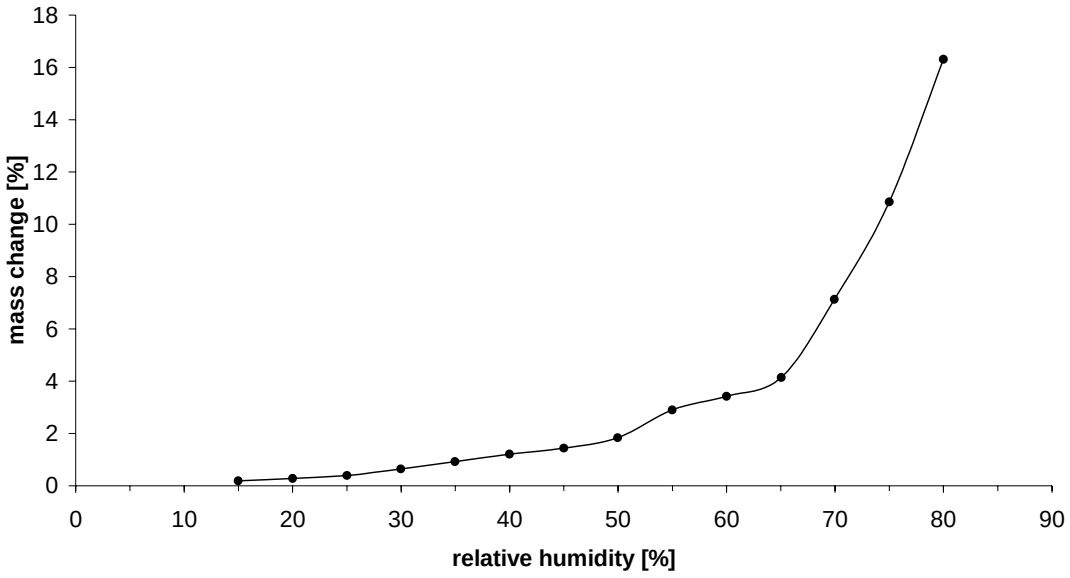


Figure 2: Adsorption isotherm for the fly ash material obtained with a IGAsorp moisture sorption analyser (Hiden Isochema Ltd., UK)

Furthermore, laboratory no. 12 observed that results from oven drying techniques varied greatly when different drying agents were used during the cool down phase and consequently applied the Karl-Fischer technique. These findings also support the results of the adsorption isotherm measurements.

Taking into account all these difficulties, a dry-mass correction protocol is recommended for the use of the material (see section 8:

Instructions for use). A drying temperature of 105 °C and a drying time of at least two hours is chosen, as this close to the drying methods that most laboratories used in the characterisation. Further, an additional uncertainty contribution is added to the final uncertainties of the certified values to take into account the uncertainty in the dry mass corrections and the variation in the methods actually applied. This uncertainty contribution is estimated by the standard deviation of the different water contents reported. As a result, an additional uncertainty contribution of 0.7 % is included in the combined uncertainty of the certified values.

6.3. Evaluation of results

The data obtained from the participating laboratories was subjected to statistical outlier tests (Cochran test, Dixon test, Nalimov-t-test). Based on these tests, a visual inspection of the data and an evaluation of the performance with the ‘quality control’ samples, some outliers could be identified. After a discussion with the laboratories concerned during the certification meeting and further examination of the methods applied, some contributions were withdrawn or excluded from the evaluation. No values were excluded from the evaluation for statistical reasons alone, data were only excluded if a sound technical reason was given.

The mean of the accepted laboratory means of the characterisation and the uncertainty of the characterisation u_{char} are listed in Table 7. The contribution of the characterisation to the uncertainty of the certified value is estimated as the standard deviation of the mean of the laboratory means.

Table 7: Summary of data of the characterisation

Analyte	Number of valid datasets	Mean of laboratory means (mg / kg)	u_{char} / %
As	6	54	2.7
Cd	9	226	1.5
Co	5	26.7	2.4
Cr	6	810	1.8
Cu	9	1050	1.2
Fe	6	13100	1.0
Hg	5	1.60	5.5
Mn	4	730	1.6
Ni	5	117	0.9
Pb	5	5000	1.3
Sb	6	850	2.5
Se	6	18.3	2.5
Tl	4	1.32	2.8
V	4	35	4.6
Zn	6	16800	0.5

The data presented in has been obtained after removal of certain datasets as a consequence of a detailed technical discussion that is summarised in Table 8.

Table 8: Detailed discussion of technical details

Lab code	Method acronym	Elements concerned	Discussion of technical details
07	All	All	Aqua regia leach was used instead of total digestion, typically, this leads to lower results. All results were excluded from evaluation.
03	All	All	The lab always used the same digest when different methods of analysis were applied. All results of that lab are used if no other problem was identified, nevertheless, they are only counted as one independent result (e.g. when calculating the standard

Lab code	Method acronym	Elements concerned	Discussion of technical details
			deviation of the mean).
04	All	All	The lab delivered some incomplete sets of data, or used different digestions within one dataset, for As, an interference by Ag^{110} was not considered, for some elements performance with the quality control sample was poor, consequently, all results are excluded from evaluation
02	HG-AFS	As	Results are detected as outlier by the Nalimov-t-test at a probability of 0.05. The samples have been digested with the addition of HF at 190 °C for 16h. There is some evidence that prolonged heating with HF can lead to the formation of volatile AsF_5, resulting in losses of As. The result is therefore excluded from evaluation.
06	INAA	Cd	Lab expressed doubts about their calibration standard, but the results are retained for evaluation as the measurement of the quality control sample shows no evidence of a calibration problem.
01	ETAAS	Co	Lab reported results with a large scatter, indicating a possible lack of control, results are excluded from evaluation
11	ID-ICP-MS	Cr	Lab showed poor performance with quality control sample, result excluded from evaluation
03	ICP-OES	Cr	Lab reported low "recovery" from digestion and withdrew results
03	ICP-OES	Cu	Result is detected as outlier by different outlier tests, as there is not technical reason for excluding this lab, the results are retained
02	RNAA	Ni	Lab showed poor performance with quality control sample, result excluded from evaluation

05	ICP-OES	Ni	Result is detected as outlier by different outlier tests. The lab used a lithiumtetraborate fusion for sample preparation. There is a possibility that insoluble Ni oxides are formed during the fusion, leading to losses of Ni. The results are therefore excluded from evaluation.
01	ETAAS	Pb	Lab reported results with a large scatter, indicating a possible lack of control, results are excluded from evaluation
03	ICP-OES ICP-MS	Pb	Lab reported problems with digestion and/or calibration and withdrew results
11	ID-ICP-MS	Pb	Lab showed poor performance with quality control sample, result excluded from evaluation
08	INAA	Sb	Lab showed poor performance with quality control sample, result excluded from evaluation
02	RNAA	Se	Result is detected as outlier by the Nalimov-t-test at a probability of 0.05, as there is not technical reason for excluding this lab, the results are retained
11	ID-ICP-MS	Tl	Lab reported an interference and withdrew results
05	ICP-OES	Zn	Result is detected as outlier by different outlier tests. The lab used a lithiumtetraborate fusion at 1100 °C for sample preparation. There is a possibility that some Zn can evaporate during the fusion (boiling point of Zn: 907°C), leading to losses of Zn. The results are therefore excluded from evaluation.

7. Certified / indicative values

7.1. Certified values and uncertainties

The certified values result from the characterisation study (Table 7). The uncertainty of the certified values contains contributions of the homogeneity u_{bb}, the long-term stability u_{lts}, the characterisation u_{char} and of the dry mass correction $u_{dry\ mass}$

The different contributions to the uncertainty are then combined using the following equation:

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{dry\ mass}^2}$$

The expanded uncertainty of the certified value U_{CRM} is calculated with a coverage factor of k = 2, representing a level of confidence of approximately 95%.

Table 9: Certified values and their uncertainties for BCR-176R

Analyte	Certified value [mg/kg]	U_{CRM} [mg/kg] k = 2	U_{CRM} [%]	u_{char} [%]	u_{bb} [%]	u_{lts} [%]	$u_{dry\ mass}$ [%]
As	54	5	7.7	2.7	1.59	2.2	0.7
Cd	226	19	8.2	1.5	3.56	1.2	0.7
Co	26.7	1.6	5.7	2.4	0.86	1.1	0.7
Cr	810	70	7.9	1.8	0.93	3.3	0.7
Cu	1050	70	5.9	1.2	2.3	1.2	0.7
Fe	13100	500	3.4	1.0	0.74	0.9	0.7
Ni	117	6	4.6	0.9	1.5	1.3	0.7
Pb	5000	500	9.2	1.3	4.1	1.5	0.7
Sb	850	50	5.6	2.5	0.5	0.9	0.7
Se	18.3	1.9	10.1	2.5	2.01	3.8	0.7
Tl	1.32	0.21	15.2	2.8	3.69	6	0.7
Zn	16800	400	2.4	0.5	0.41	0.7	0.7

For Tl, only 4 valid datasets are available. These methods include ID-TIMS and ID-ICP-MS, which are confirmed by conventional ICP-MS measurements. Isotope dilution techniques have the potential to deliver SI traceable results. Therefore it is acceptable to certify the Tl content based on four datasets only.

7.2. Indicative values and uncertainties

The data obtained for the elements Hg, Mn and V did not allow a certification.

For Hg, only 5 valid data sets are available, which scatter more than for all other elements (u_{char} of 5.5 %, while all other elements for which certified values could be derived have an u_{char} below 3%). For Mn and V only 4 valid datasets are available, which is not sufficient to certify the value according to the rules applied at IRMM. For both elements, also none of the laboratories use e.g. an isotope dilution method, which would have a greater potential of delivering high quality data.

Table 10: Indicative values and their uncertainties for BCR-176R

Analyte	Indicative value (mg/kg)	U_{CRM} (mg/kg) k = 2	U_{CRM} (%)	u_{char} (%)	u_{bb} (%)	u_{lts} (%)	$u_{dry\ mass}$ *(%)*
Hg	1.60	0.23	14.1	5.5	4.04	1.7	0.7
Mn	730	50	6.1	1.6	1.65	1.8	0.7
V	35	6	15.0	4.6	4.37	4	0.7

7.3. Additional material information

Some additional data are available from k_0-NAA for some elements. As this data have been obtained by one method only it is given as "additional material information".

Table 11: Additional material information for BCR-176R

Analyte	Value as measured by k_0-NAA [mg/kg]	RSD of k_0-NAA results [%] (*n*=32)
Ag	33.1	2.0
Au	0.604	5.3
Ba	4650	2.4
Br	836	1.6
Ce	47.7	3.5
Cs	8.27	1.6
Eu	0.868	5.9
Hf	4.85	2.3
La	30.2	2.6
Na	34800	2.7
Rb	102	2.6
Sc	2.91	2.6
Ta	2.02	5.9
Th	5.28	1.7
W	28.3	4.6

7.4. Metrological traceability

Traceability of the certified values to the SI is ensured through the set-up of the characterisation. The participating laboratories used a number of different methods for the sample preparation as well as for the final determination, thus eliminating any possibility of method dependent results. In addition, different calibrants have been used, including commercial standard solutions, CRMs and in-house gravimetrically prepared calibrants. Most laboratories also used matrix CRMs for quality control. In addition, the participating laboratories received a bottle of the previous BCR-176 as a quality control sample. This set-up ensures that all individual result obtained from the participating laboratories are SI-traceable. Consequently, the certified values are SI traceable.

7.5. Commutability

Commutable CRMs must exhibit the same analytical behaviour for given methods as a real laboratory sample. The laboratories participating in the characterisation study have been selected such as to provide a large variety of analytical methods, regarding digestion, calibration and detection. The good agreement between the

results obtained shows the commutability of the material. Nevertheless it has to be kept in mind that the certified reference materials might show a behaviour different from real samples, in particular during digestion, due to their small particle sizes in contrast to the possibly larger particle sizes encountered for real laboratory samples, and due to the intensive processing that this CRM has undergone.

8. Instructions for use

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

Storage of the material

Samples should be stored in the dark at 18 °C. Care should be taken to avoid moisture pickup once the bottles are open, as the material is hygroscopic. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

Use of the material

The bottles should be shaken for at least two minutes before opening to ensure re-homogenisation of the content.

When the material is analysed, care should be taken to analyse the total content of elements. From the characterisation of the material it could be seen that a simple aqua regia leach will result in low recoveries. For wet digestions the use of HF in the acid mixture is recommended while care should be taken not to loose volatile fluorides.

Dry mass correction

Dry mass determination should be carried out on separate subsamples. Weighing of the samples for dry mass determination and the analysis must be done at the same time to avoid differences in moisture due to the hygroscopicity of the fly ash. Dry mass determination should be carried out by drying in a ventilated oven at 105 °C for at least 2 hours, until constant weight is reached.

Comparing an analytical result with the certified value

A result is unbiased if the combined uncertainty of measurement and certified value covers the difference between the certified value and the measurement result. To this end, the following steps are necessary:

1) Assessment of the measurement uncertainty: This uncertainty will depend whether accuracy of one individual result or accuracy of a method in general shall be assessed.

Measurement uncertainty can be estimated from reproducibility data obtained during method validation. These reproducibility data do not comprise uncertainty of the calibration. This uncertainty has to be added. The uncertainty is then estimated as

$$u_{meas} = c\sqrt{u_R^2 + u_{st}^2}$$

u_{meas} standard measurement uncertainty

c concentration for which the uncertainty should be evaluated

u_R relative uncertainty due to reproducibility (as taken from the validation study)

u_{st} relative uncertainty of the calibration standard (mainly purity).

u_{st} can be ignored if it is < 1/3 u_R

2) Take the standard uncertainty of the certified value of the material in question (u_{CRM}). E.g. for As in BCR-176R, this would be 2.5 mg/kg.
3) Combine the two uncertainties as $u_c = \sqrt{u_{meas}^2 + u_{CRM}^2}$
4) The method is not significantly biased if the difference between the measured result and the certified value is smaller than 2 u_c.

A more detailed explanation can also be found in the ERM Application Note 1 [8].

Use in quality control charts

The material can be used for quality control charts. Different CRM-units will give the same result as heterogeneity was found to be negligible.

Use as a calibrant

It is not recommended to use matrix materials such as BCR-176R as calibrants. If used nevertheless, the uncertainty of the certified value shall be taken into consideration in the final estimation of measurement uncertainty.

References

[1] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste. Official Journal of the European Union L 332 (2000) 91

[2] private communication (IRMM internal report GE/R/RM/08/98)

[3] T. P. J. Linsinger, J. Pauwels, A. M. H. van der Veen, H. G. Schimmel, A. Lamberty, Accred. Qual. Assur., 2001, 6, 20-25.

[4] K. C. Friese, K. H. Grobecker, U. Wätjen, Fresenius J. Anal. Chem., 2001, 370, 843-849.

[5] private communication (IRMM internal report GE/R/RM/12/01).

[6] J. Pauwels, C. Vandecasteele, Fresenius J. Anal. Chem., 1993, 345, 121-123.

[7] T. P. J. Linsinger, J. Pauwels, A. Lamberty, H. G. Schimmel, A. M. H. van der Veen, L. Siekmann, Fresenius J. Anal. Chem., 2001, 370, 183-188.

[8] ERM application notes (internet at www.erm-crm.org)

Acknowledgements

The authors would like to thank T. Linsinger and R. Zeleny (IRMM, BE) for the reviewing of the certification report, as well as the experts of the Certification Advisory Panel ‘Elements and inorganic ions’, O. Donard (CNRS / Université de Pau et des pays de l’Adour, FR), L. Jorhem (Livsmedelsverket, SE) and H. Muntau (Ranco, IT) for their constructive comments.

Annexes

Annex 1: Summary of methods used

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
01	ID-ICP-MS	Cu, Cd, Pb	0.1	4 mL HNO_3, 3 mL HF in a closed vessel, heated for 24 h at 200 °C	IRMM-622 (Cd), IRMM-632 (Cu), SRM-991 (Pb)	Q-ICP-MS, isotopes measured: ^{63,65}Cu, ^{111,113,115,118}Cd, ^{206,207,208}Pb
	ETAAS	Cd, Co, Cu, Ni, Pb	0.2	2 mL H_2O, 4 mL HNO_3, 4 mL HCl, 30 min pre-digestion, addition of 2 mL HF, 60 min digestion in a microwave	SRM 3108 (Cd), SRM 3113 (Co), SRM 3114 (Cu), SRM 3136 (Ni), PE standards (Cd, Co, Cu, Ni, Pb), CRDL standard (Pb)	ETAAS, Zeeman background correction, lines used: Cd 228.8 nm, Co 240.7 nm, Cu 324.8 nm, Ni 232.0 nm, Pb 283.3 nm
	FAAS	Zn	0.2		SRM 3168a and PE standard (Zn)	FAAS, deuterium background correction, line used: Zn 213.9 nm
	k_0-NAA	As, Cd, Co, Cr, Fe, Sb, Se, Zn	0.6 - 0.7	Not applicable	IRMM-530	7 h irradiation, thermal neutron flux of $3 \cdot 10^{11}$ $cm^{-2}s^{-1}$

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
02	CVAAS	Hg	0.25	Wet pressure ashing in HNO_3/$HClO_4$/HF for 16 h at 190 °C	Baker ICP Hg standard	CVAAS, line used: Hg 254 nm
	HGAFS	As	0.25	Wet pressure ashing in HNO_3/$HClO_4$/HF for 16 h at 190 °C, addition of HCl, HNO_3, H_2SO_4 and evaporation to 5 mL, dilution with 0.1 M HCl	Baker ICP As standard	HGAFS, line used: As 193.7 nm
	ID-TIMS	Cd, Cr, Cu, Fe, Ni, Pb, Tl, Zn	0.2 – 0.3	Wet pressure ashing in HNO_3/$HClO_4$/HF for 48 h at 180 °C, evaporation to dryness, redissolution, anion exchange separation (Cd, Cr, Fe, Pb, Zn), electroplating (Cu), anion exchage separation with subsequent cation exchange separation and electrodeposition (Ni)	^{112}Cd, ^{53}Cr, ^{65}Cu, ^{57}Fe, ^{62}Ni, ^{206}Pb, ^{203}Tl, ^{68}Zn spikes calibrated with two different standards each	TIMS, silicagel/H3PO4 (Cd, Cu, Ni, Pb, Tl, Zn), silicagel/H3BO3 (Cr, Fe) single filament technique, isotopes measured: ^{111,112,114}Cd, ^{52,53}Cr, ^{63,65}Cu, ^{56,57}Fe, ^{58,60,62}Ni, ^{206,207,208}Pb, ^{203,205}Tl, ^{64,68}Zn
	INAA	Mn, V	0.5 – 0.6 Hg, Se: 0.1 Ni: 0.2	Not applicable	SRM 3171a Hg, Ni: external calibration using Merck standard Se: SRM 3172A	Low flux reactor, thermal neutron flux $3 \cdot 10^{11}$ $cm^{-2}s^{-1}$, low energy gamma ray spectrometer Ni: Well-type 60 % HPGe detector Se: 17 % HPGe gamma-ray spectrometer
	RNAA	Cd, Hg, Ni, Se		After irradiation: wet pressure ashing in HNO_3/$HClO_4$/HF for 24 h at 180 °C, anion exchange separation Se: ion exchange separation on inorganic ion exchanger		

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
03	AFS	Hg	0.5	Microwave assisted closed vessel wet digestion using HCl, HNO_3, HF and H_3BO_3	Merck Hg standard solution	AFS
	ICP-OES	As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sb, Se, Tl, V, Zn	0.5		Merck and Spex standard solutions	ICP-OES, axially viewed, lines used: As: 189 nm, Cd: 214 nm, Co: 230 nm, Cu: 324 nm, Fe: 259 nm, Mn: 257 nm, Ni: 232 nm, Pb: 220 nm, Sb: 206 nm, Se: 196 nm, Tl: 190 nm, V: 292 nm, Zn: 213 nm
	ICP-MS	As, Co, Mn, Pb, Sb, Se, Tl, V	0.5			Q-ICP-MS, isotopes measured: ^{75}As, ^{59}Co, ^{55}Mn, ^{208}Pb, ^{121}Sb, ^{82}Se, ^{205}Tl, ^{51}V
	ICP-OES	Cr	0.5	Microwave assisted wet digestion in semi-open vessels with HF, H_2SO_4, HNO_3 and H_3BO_3	Merck and Spex standard solutions	ICP-OES, axially viewed, lines used: nCr: 205 nm

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
04	ETAAS	Cr, Mn, Tl, V	0.1	Microwave digestion using HF, HNO_3, HCl, H_2O_2, for 1 h at 200 °C and $LiBO_2$ fusion	Merck and Johnson Matthey standard solutions	ETAAS, lines used: Cr 357 nm, Mn 279 nm, Tl 276 nm, V 318 nm
	CVAAS	Hg	0.02 and 0.1	High pressure bomb digestion using HF and HNO_3 for 2-6 h at 150 °C and microwave digestion using $HF/HNO_3/HCl/H_2O_2$ for 1 h at 200 °C		CVAAS, line used: Hg 254 nm
	HGAAS	Se	0.05 and 0.1	Pressure digestion with HNO_3 for 3 h at 150 °C and NaOH fusion		HGAAS, line not specified
	ICP-OES	Tl	0.1 and 0.25	Microwave digestion using HF, HNO_3, HCl, H_2O_2, for 1 h at 200 °C and $LiBO_2$ fusion		ICP-OES, line used: Tl 351 nm
	ICP-MS	Hg	0.02 and 0.1	High pressure bomb digestion using HF and HNO_3 for 2-6 h at 150 °C and microwave digestion using $HF/HNO_3/HCl/H_2O_2$ for 1 h at 200 °C		ICP-MS (high resolution instrument), used resolution not specified, isotopes measured: $^{200,\ 201,202}Hg$, ^{103}Rh as internal standard
	INAA	As,Cr, Hg, Ni, Sb	0.06 – 0.15	Samples were irradiated in closed quartz ampoules, one was measured directly, others were opened and the sample dissolved in oxidising media, separated from ^{24}Na	Fluxmonitor and in-house prepared element standards	Neutron flux $3.2 \cdot 10^{13}$ thermal, $2.4 \cdot 10^{12}$ epithermal, $3.4 \cdot 10^{12}$ fast intrinsic germanium coaxial detector

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
05	CVAAS	Hg	0.005 and 0.1	Drying at 120 °C, combustion at 900 °C, Hg is concentrated on a gold wire	Spex standard solution	CVAAS, wavelength 254 nm
	ICP-OES	Cd, Cu, Pb, V	0.07-0.1	Pressure digestion with $HF/HNO_3/HClO_4$ for 72 h at 90 °C, evaporation to dryness and redissolution in HNO_3	Spex standard solutions, checked against solutions prepared from pure metals or metal salts	ICP-OES, lines used: Cd: 214 nm, Cr: 205 nm, Cu: 224 nm, Fe: 259 nm, Mn: 257 nm
		Cr, Fe, Mn, Ni, Zn	0.08 – 0.1	Fusion with lithiumtetraborate at 1100 °C for 2 h		
	ICP-MS	As, Co, Pb, Se, Tl,	0.06 – 0.1	Pressure digestion with $HF/HNO_3/HClO_4$ for 72 h at 90 °C, evaporation to dryness and redissolution in HNO_3		ICP-MS (high resolution instrument), isotopes measured: ^{75}As, ^{59}Co, $^{78,82}Se$, $^{203,205}Tl$ (high resolution); $^{121,123}Sb$ (medium resolution); $^{206,207,208}Pb$ (low resolution)
		Sb	0.08 – 0.1	Fusion with lithiumtetraborate at 1100 °C for 2 h		

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
06	INAA	As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Sb, Se, V, Zn	0.1 – 0.35	Not applicable	Johnson Matthey Specpure As_2O_3, Cd, Co, $K_2Cr_2O_7$, Cu, Fe_2O_3, Hg, MnO_2, Ni, Sb_2O_3, SeO_2, V_2O_5, Zn verified with: SRM 1632a, SRM 1633, BCR-176, BCR 146R, SRM 1633a, SRM 1648, BCR 144R, SRM 1645	Neutron flux: $4 \cdot 10^{12}$ $cm^{-2}s^{-1}$, Ortec intrinsic Ge detector
	RNAA	Cu	0.3 - 0.35	Post-irradiation digestion with HNO_3/HF at 160 °C, fixation of Cu on CuS		

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
07	ICP-MS	Zn, V, Tl, Se, Pb, Ni, Mn, Fe, Cu, Cr, Co, Cd,	2	Digestion with aqua regia under reflux for 2 h	Commercially available standard solutions	ICP-MS (quadrupole), isotopes measured: ^{64}Zn, ^{51}V, ^{205}Tl, ^{82}Se, ^{208}Pb, ^{60}Ni, ^{55}Mn, ^{54}Fe, ^{63}Cu, ^{52}Cr, ^{59}Co, ^{114}Cd
	CVAAS	Hg	2			CVAAS, lines used: Hg 254 nm
	ICP-OES	Zn, V, Mn, Fe, Co				ICP-OES, lines used: Zn 213 nm, V 292 nm, Mn 257 nm , Fe 260 nm, Co 229 nm
	FAAS	Zn, Pb, Ni, Mn, Fe, Cu, Cd	2			FAAS: lines used: Zn 213 nm, Pb 217 nm, Ni 232 nm, Mn 279 nm, Fe 248 nm, Cu 325 nm, Cd 229 nm
	HGAAS	Se, Sb, As	2			HGAAS with FIAS manifold, lines used: Se 196 nm, Sb 218 nm, As 194 nm

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
08	INAA	As, Cr, Hg, Sb	0.5	Not applicable	External standards prepared from high purity metals and salts (As, $Cr(NO_3)_3$, Sb_2O_3 from Merck, Aldrich, Baker, checked against SRM 3103a and Aldrich standard solutions	Neutron flux: $300 \cdot 10^{-11} cm^{-2} s^{-1}$, Gamma-X-Ge-detector
09	ID-ICP-MS	Cu, Pb	0.04	Closed vessel microwave digestion, 2 mL HNO_3, 1 mL HF, 1 mL H_2O_2	^{65}Cu enriched spike solution (spectrascan) and SRM 991, characterised by reverse isotope dilution	ICP-MS (quadrupole), $^{63,65}Cu$ and $^{208,206}Pb$ measured
10	k_0-NAA	As, Co, Cr, Fe, Sb, Se, Zn	0.2	Not applicable	IRMM-530 flux monitor	Thermal to epithermal neutron flux ration f = 25.1, epithermal shape factor alpha = -0.0045 HPGe detector

Lab code	Method acronym	Elements	Sample mass (g)	Sample preparation	Calibrants	Instrumentation and measurement method
11	ID-ICP-MS	Cd, Cr, Cu, Ni, Pb, Sb, Tl	0.1	Closed vessel microwave digestion with HNO_3/HCl/HF for 14 min, addition of H_3BO_3, 10 min digestion	^{111}Cd, ^{53}Cr, ^{65}Cu, ^{62}Ni, ^{206}Pb, ^{121}Sb, ^{203}Tl enriched spike solution, spike calibrated by reverse isotope dilution against solutions prepared from high purity metal, SRM 981 and 982 for mass bias correction of Pb	ICP-MS (sector field instrument), isotopes measured (low resolution): $^{111,113}Cd$, $^{121,123}Sb$ (medium resolution): $^{53,52}Cr$, $^{65,63}Cu$, $^{62,60}Ni$, $^{208,206}Pb$, $^{203,205}Tl$
	ICP-MS	Hg			Calibration solution prepared from high purity $HgCl_2$	ICP-MS (sector field instrument), isotopes measured (low resolution): ^{202}Hg
12	ID-ICP-MS	Tl	1 - 2	Closed vessel microwave digestion, using 10 mL HNO_3 and 2 mL H_2O_2, 35 min at max. 220 °C, addition of 3 mL HCl, 2 mL HF, 35 min at max 220 °C, removal of HF by evaporation, anion exchange separation	^{203}Tl used as spike, characterised by reverse isotope dilution	ICP-MS (multi-collector),

Annex 2: Data from homogeneity studies

Table 12: Data from homogeneity study for As, Cd, Co, Cr, Fe, Hg, Pb, Sb and V (wb: data obtain on subsamples of one bottle, bb: data obtained on subsamples from different bottles, data expressed in mg/kg)

	As k_0-NAA	Cd k_0-NAA	Co k_0-NAA	Cr k_0-NAA	Fe k_0-NAA	Hg CVAAS	Pb ICP-MS	Sb k_0-NAA	V ICP-MS
wb	53.5	215	27.9	818	13185	1.33	4800	895	33.6
wb	54.8	217	27.4	804	13081	1.40	4730	885	35.7
wb	52.2	232	28.1	810	13100	1.35	4620	892	33.3
wb	52.9	211	27.8	820	13128	1.38	4810	895	34.2
wb	53.0	229	28.3	830	13397	1.33	4760	902	34.0
wb	54.8	224	28.0	825	13284	1.33	4900	896	33.4
bb	52.2	238	27.4	812	13138	1.39	4870	882	28.7
bb	50.5	234	27.3	809	12628	1.37	4460	888	28.0
bb	53.3	222	27.4	796	12859	1.38	4680	878	27.1
bb	50.6	211	27.6	805	13204	1.41	4820	882	29.3
bb	49.2	230	27.7	811	13222	1.40	4620	887	27.8
bb	49.9	239	26.8	787	13020	1.43	value missing	875	24.7
bb	54.0	206	27.3	807	12902	1.52	4090	880	27.0
bb	50.3	235	27.0	801	12873	1.35	4620	877	29.7
bb	53.5	228	27.0	791	12869	1.36	4590	872	29.0
bb	50.9	250	27.2	803	12949	1.24	4620	883	30.2
bb	52.8	256	26.9	795	12873	1.47	4050	876	27.0
bb	51.9	222	26.8	787	12751	1.50	4730	881	28.1
bb	52.1	231	27.0	794	12859	1.43	4760	877	28.3
bb	52.5	234	26.8	785	12793	1.46	4690	880	29.4
bb	51.7	234	27.6	802	12996	1.44	4680	887	28.4
bb	51.4	221	27.2	802	12939	1.36	4530	876	28.0
bb	51.3	240	26.9	804	12760	1.44	4680	868	30.7
bb	52.9	228	26.7	797	12859	1.43	4660	871	30.0
bb	51.2	217	26.9	799	12939	1.43	4600	871	29.7
bb	53.0	230	27.2	798	12836	1.31	4640	869	30.4

Table 13: Homogeneity assessment for Ni, Se and Zn using data from the stability study (data expressed in mg/kg)

bottle no	Ni ICP-MS	Se k_0-NAA	Zn k_0-NAA
0800	98.8	19.23	17108
0800	97.9	16.24	16589
0800	98.3	17.98	16552
1220	100.1	17.83	16759
1220	100.0	19.18	16919
1220	99.7	18.48	16872
2020	100.0	18.64	17061
2020	98.4	17.58	16504
2020	103.8	20.50	16618
2860	105.3	16.55	16825
2860	103.7	18.31	16702
2860	102.8	19.58	16797
3220	103.2	18.16	16797
3220	101.4	16.47	16655
3220	102.8	18.94	16665
3460	99.7	17.34	16834
3460	101.3	19.43	16514
3460	102.0	19.14	16844
3946	101.7	18.90	16712
3946	103.3	18.23	16693
3946	101.9	20.19	16372
4037	101.9	18.29	16791
4037	99.7	18.22	16674
4037	101.5	17.14	16457
4128	97.2	17.41	16948
4128	99.6	18.20	16533
4128	100.3	17.07	16363
4137	98.7	17.92	16674
4137	100.4	19.33	16372
4137	100.3	17.38	16844

Table 14: Homogeneity assessment for Cu using data from the characterisation study (data expressed in mg/kg)

Lab code, method	bottle1	bottle2
01 ETAAS	1072	1056
	1100	1037
	1080	1094
01 ID-ICP-MS	1050	1053
	1051	1047
	1054	1068
02 ID-TIMS	1077	1035
	1065	1021
	1049	1013
03 ICP-OES	963	1011
	956	978
	939	974
05 ICP-OES	1081	1075
	1072	1070
	1071	1068
06 INAA	1103	1000
	1015	1047
	1028	1098
06 RNAA	1027	1037
	1028	1087
	1007	1000
09 ID-ICP-MS	1055	1095
	1060	1088
	1058	1104
11 ID-ICP-MS	1118	1109
	1102	1079
	1074	1095

Table 15: Homogeneity assessment for Mn using data from the characterisation study (data expressed in mg/kg)

	bottle 1	bottle 2
02 INAA	687	695
	693	683
	689	708
03 ICP-OES	746	737
	797	742
	747	728
03 ICP-MS	724	717
	698	687
	747	738
04 ETAAS	726	770
	772	699
	704	735
05 ICP-OES	718	725
	726	718
	722	723
06 INAA	747	763
	727	730
	778	751

Table 16: Homogeneity assessment for Tl using data from the characterisation study (data expressed in mg/kg)

	bottle1	bottle2
02 ID-TIMS	1.329	1.322
	1.312	1.329
	1.332	1.330
03 ICP-MS	1.360	1.360
	1.310	1.350
	1.250	1.320
05 ICP-MS	1.290	1.180
	1.270	1.210
	1.250	1.200
12 ID-ICP-MS	1.408	1.404
	1.418	1.408
	1.416	1.416

Annex 3: Data from stability studies

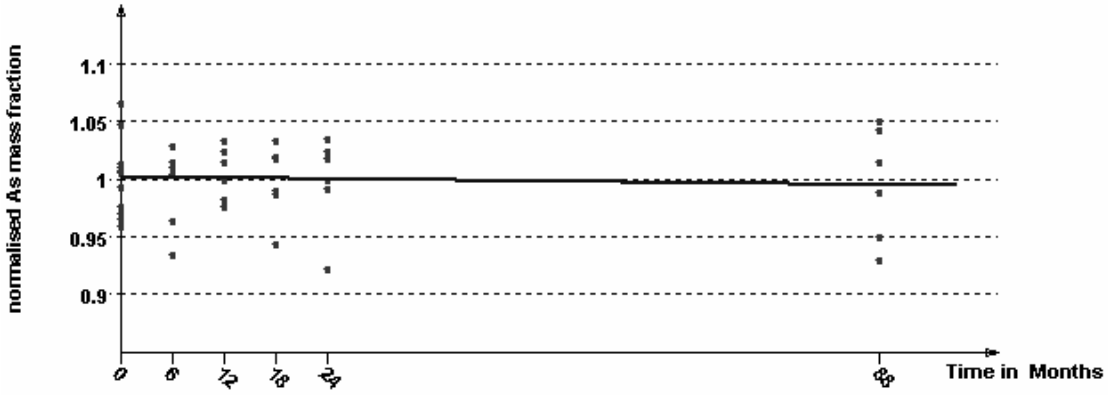


Figure 3: Stability graph for As, 18 °C

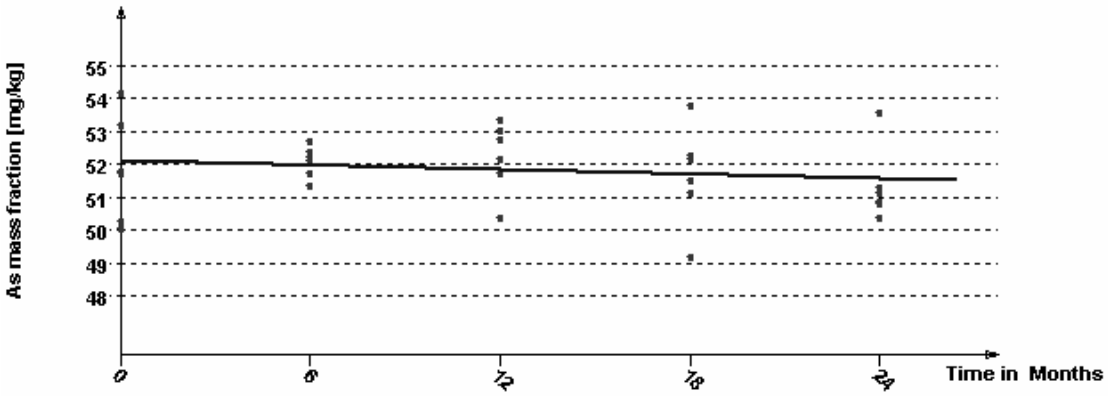


Figure 4: Stability graph for As, 40 °C

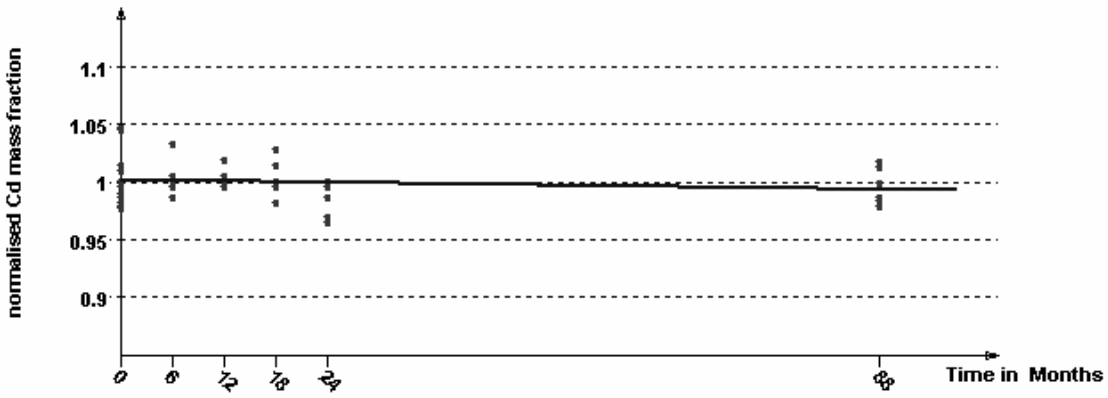


Figure 5: Stability graph for Cd, 18 °C

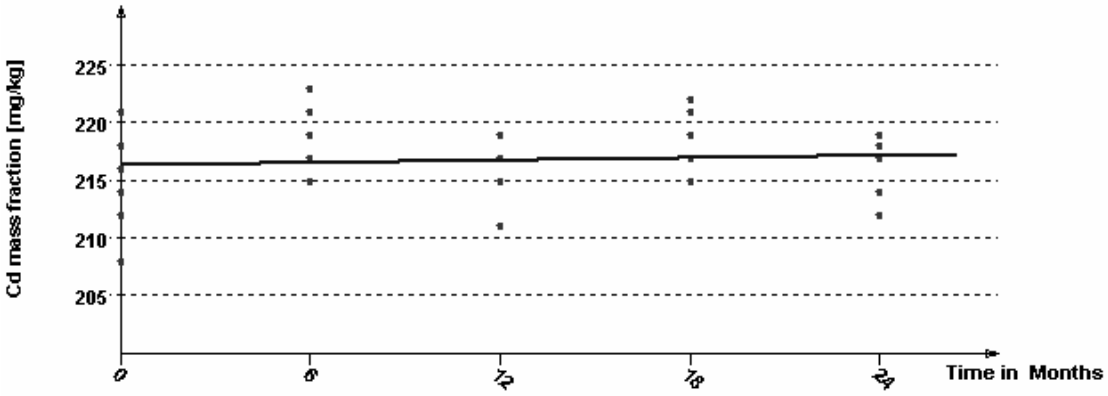


Figure 6: Stability graph for Cd, 40 °C

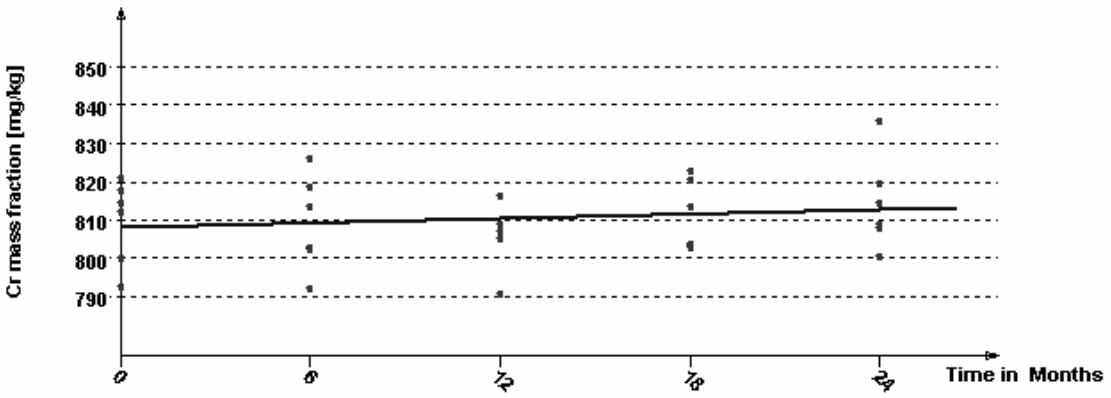


Figure 7: Stability graph for Cr, 18 °C

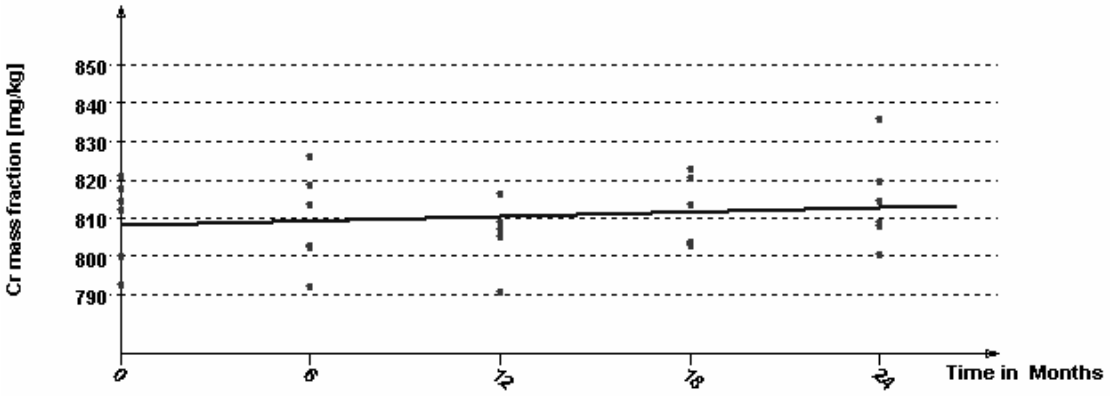


Figure 8: Stability graph for, Cr, 40 °C

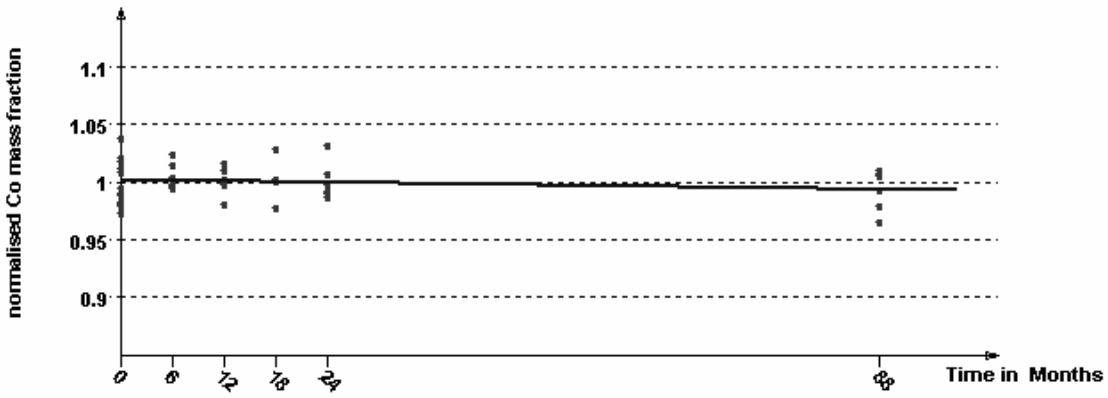


Figure 9: Stability graph for Co, 18 °C

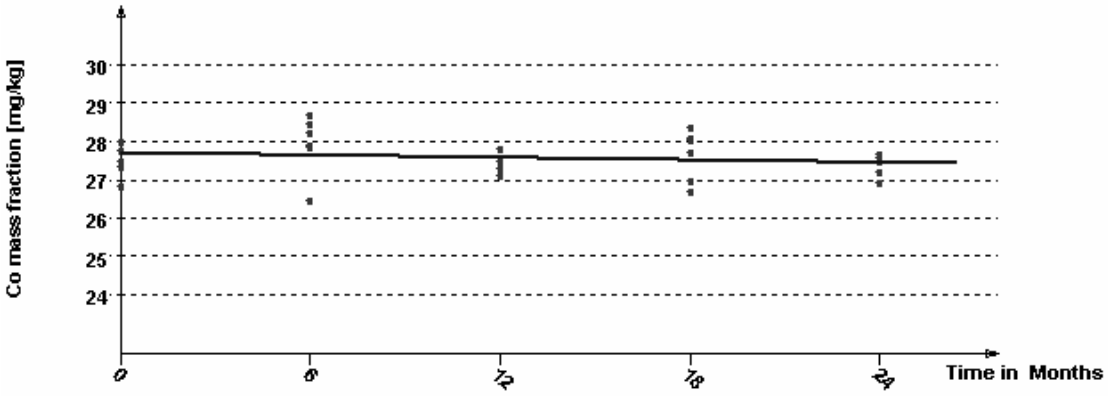


Figure 10: Stability graph for Co, 40 °C

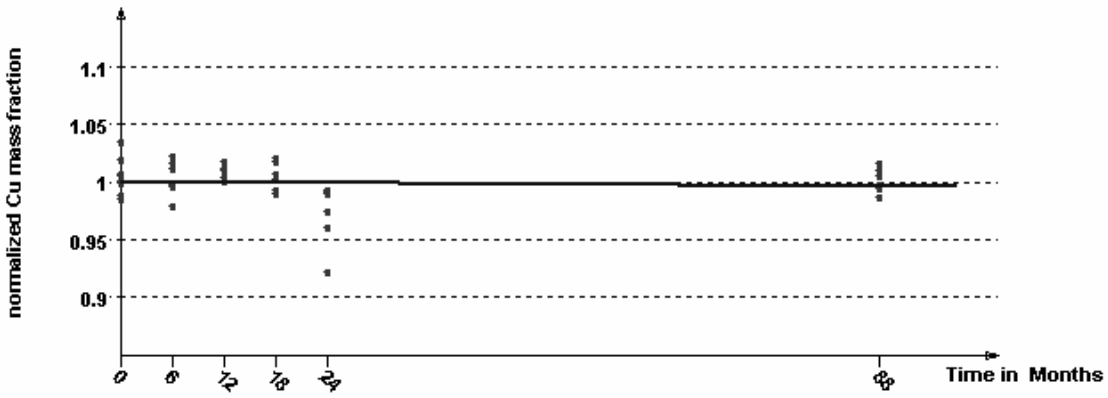


Figure 11: Stability graph for Cu, 18 °C

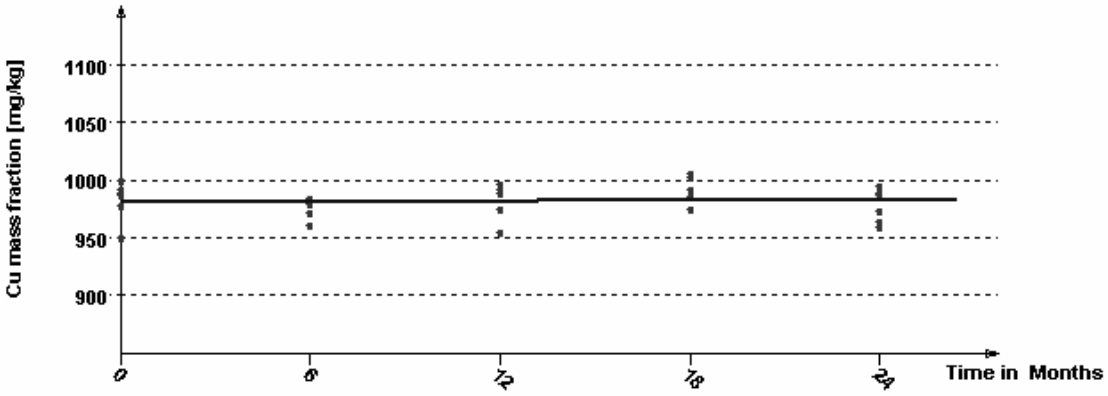


Figure 12: Stability graph for Cu, 40 °C

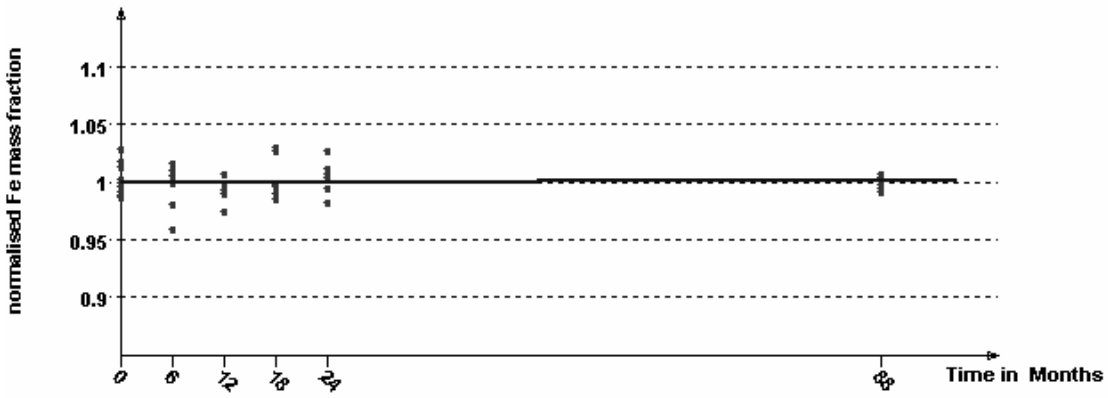


Figure 13: Stability graph for Fe, 18 °C

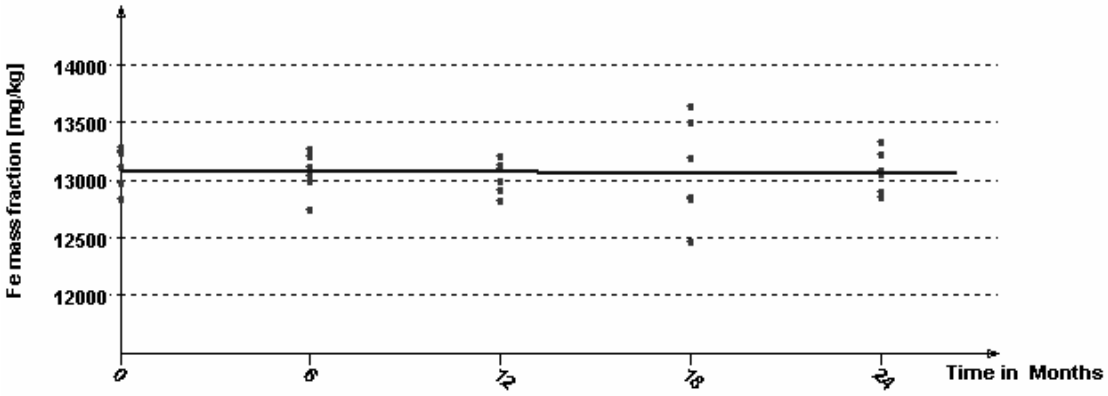


Figure 14: Stability graph for Fe, 40 °C

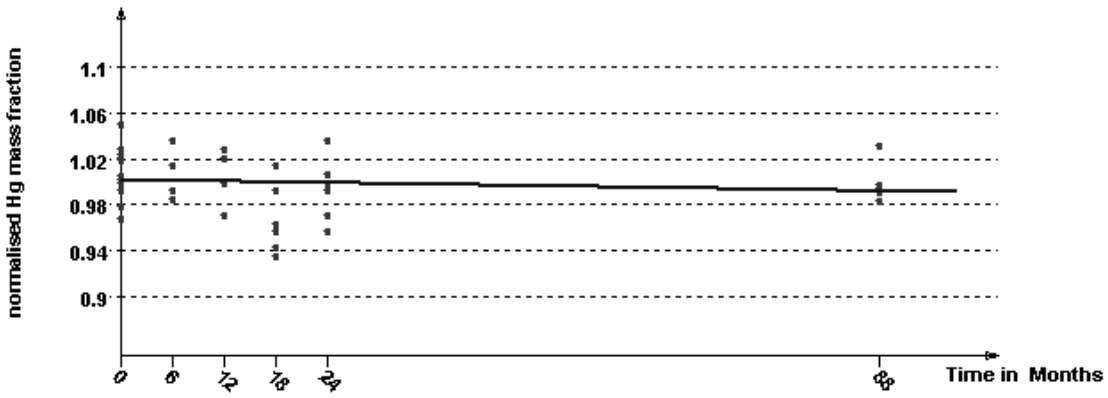


Figure 15: Stability graph for Hg, 18 °C

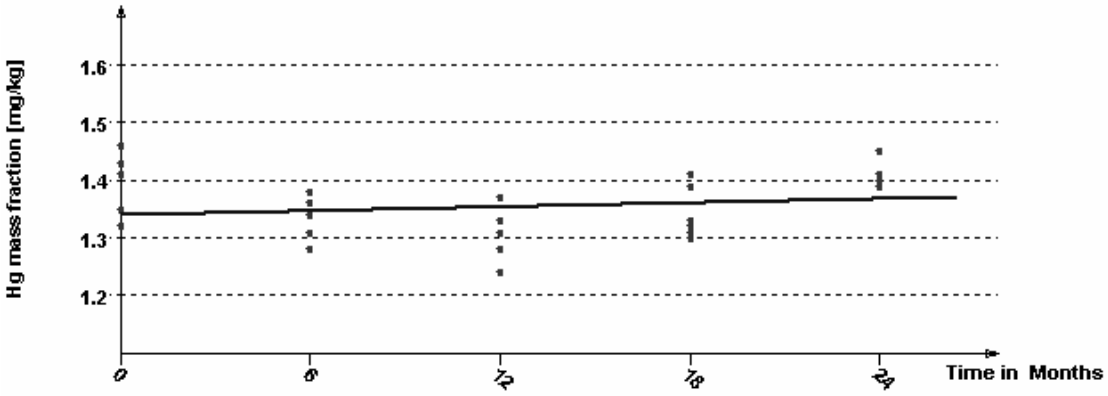


Figure 16: Stability graph for Hg, 40 °C

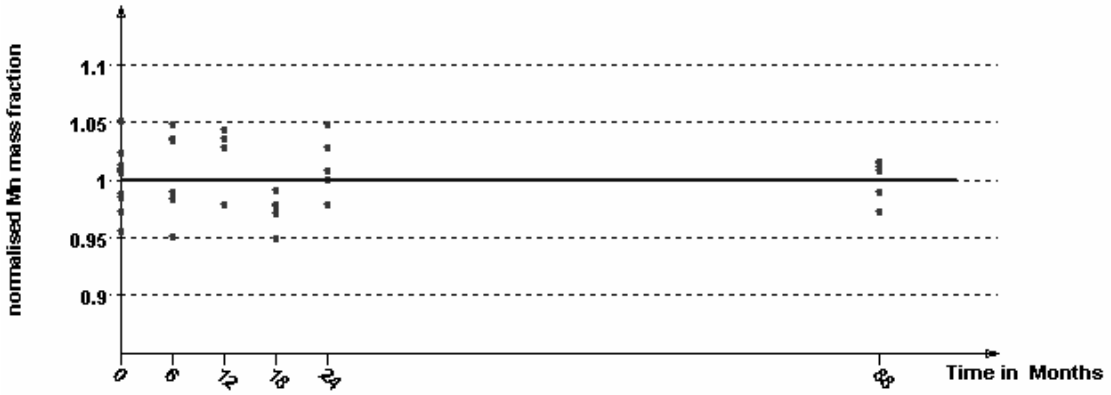


Figure 17: Stability graph for Mn, 18 °C

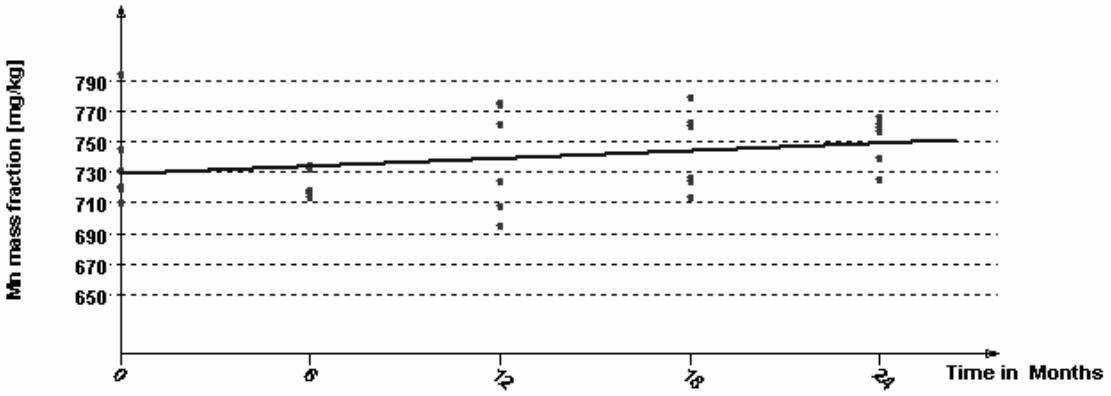


Figure 18: Stability graph for Mn, 40 °C

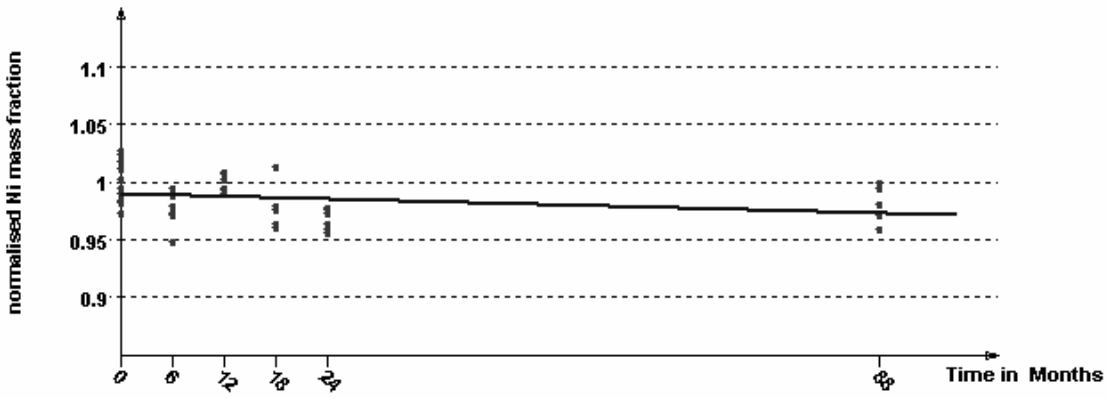


Figure 19: Stability graph for Ni, 18 °C

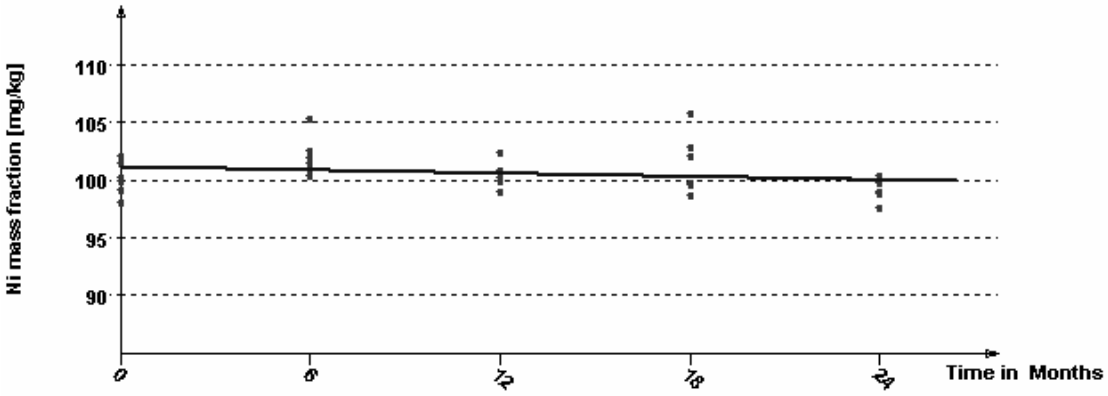


Figure 20: Stability graph for Ni, 40 °C

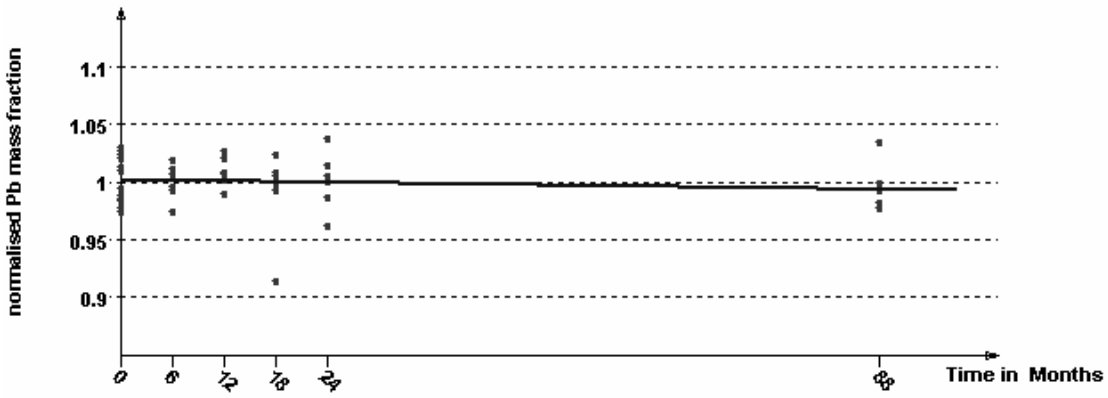


Figure 21: Stability graph for Pb, 18 °C

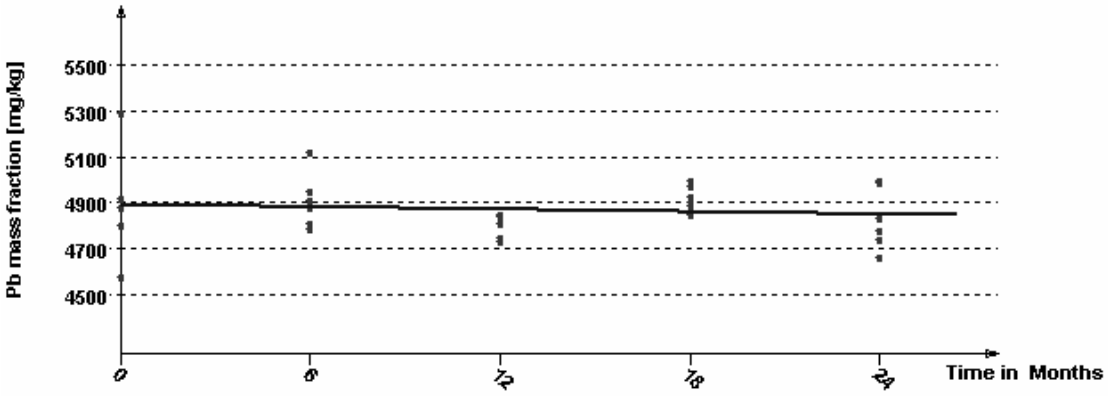


Figure 22: Stability graph for Pb, 40 °C

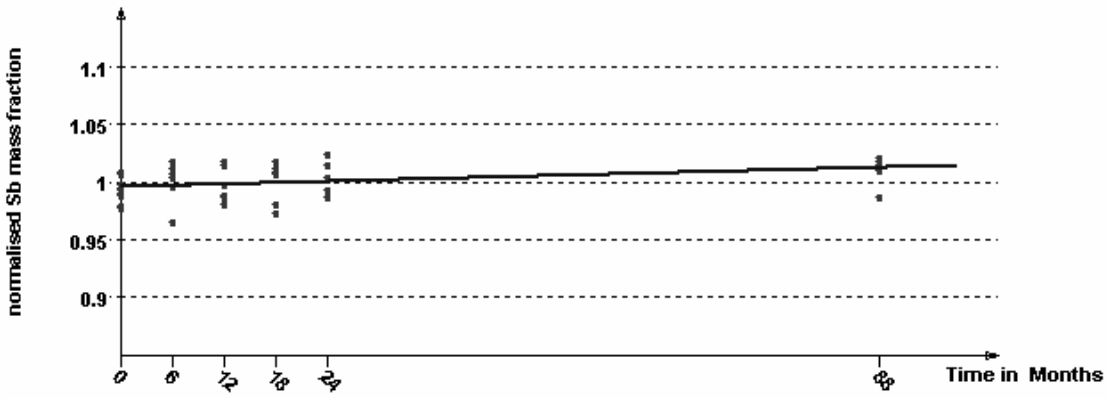


Figure 23: Stability graph for Sb, 18 °C

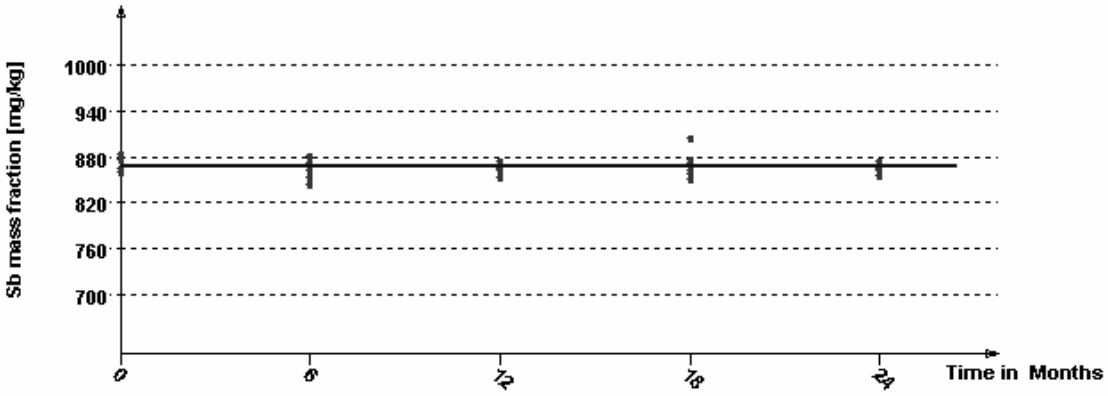


Figure 24: Stability graph for Sb, 40 °C

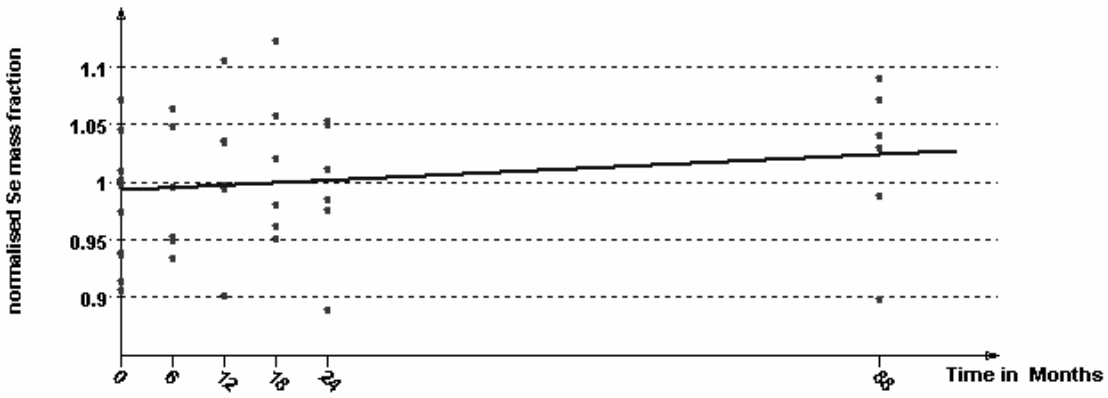


Figure 25: Stability graph for Se, 18 °C

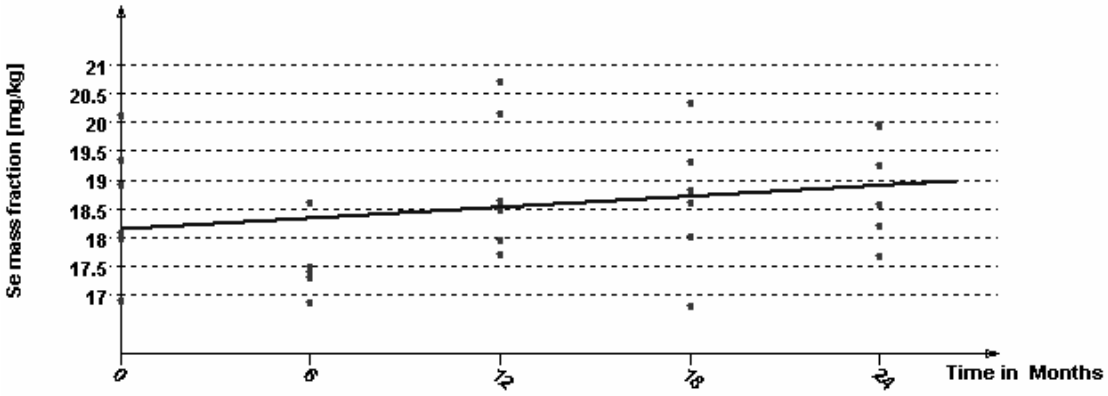


Figure 26: Stability graph for Se, 40 °C

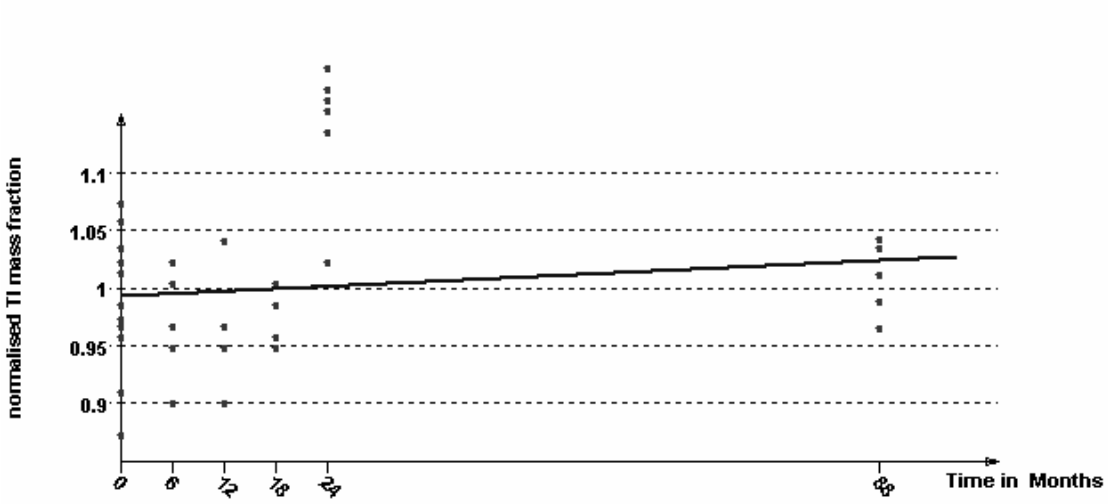


Figure 27: Stability graph for Tl, 18 °C

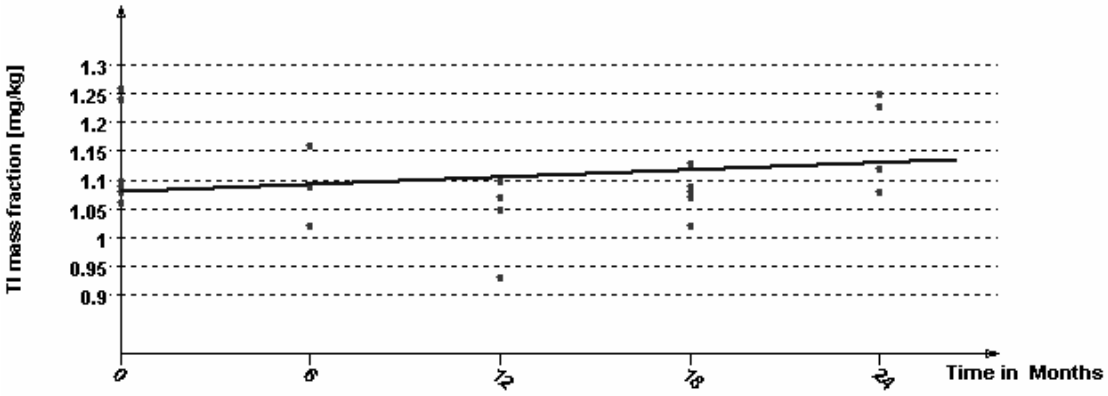


Figure 28: Stability graph for Tl, 40 °C

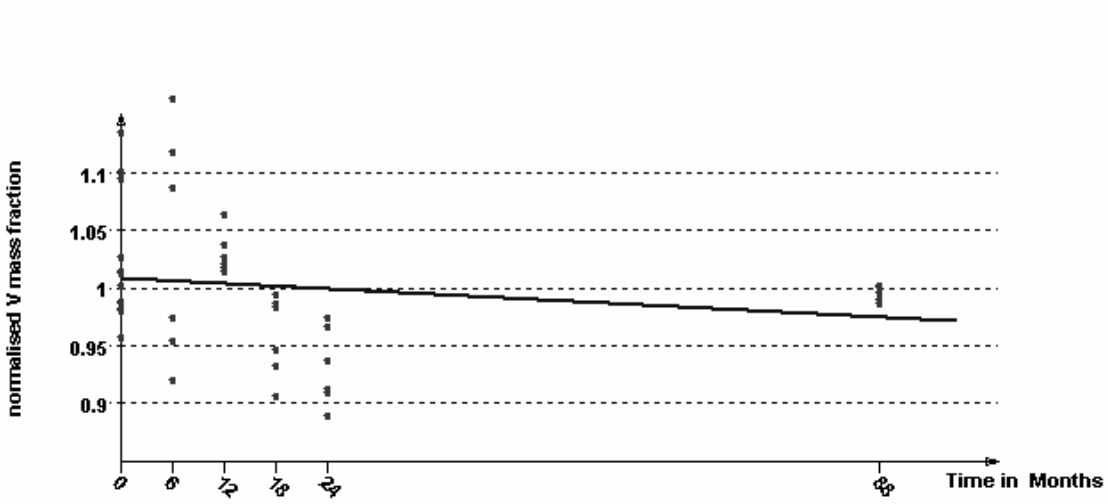


Figure 29: Stability graph for V, 18 °C

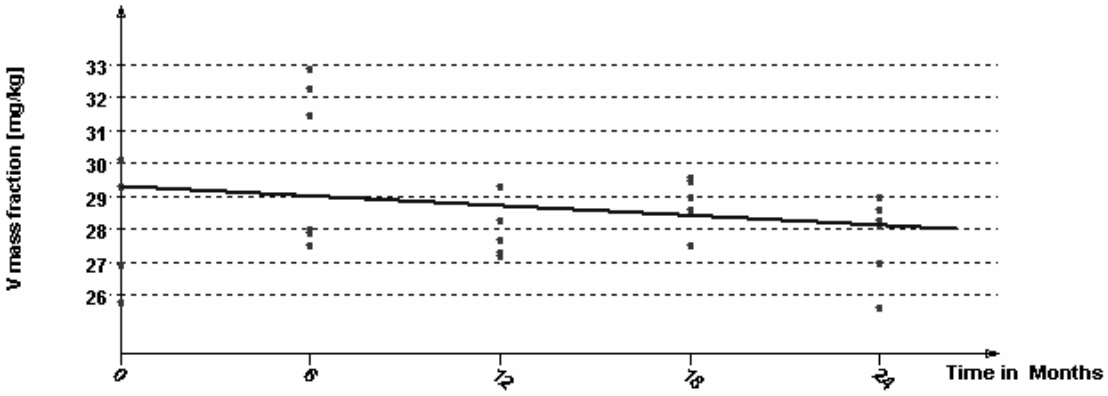


Figure 30: Stability graph for V, 40 °C

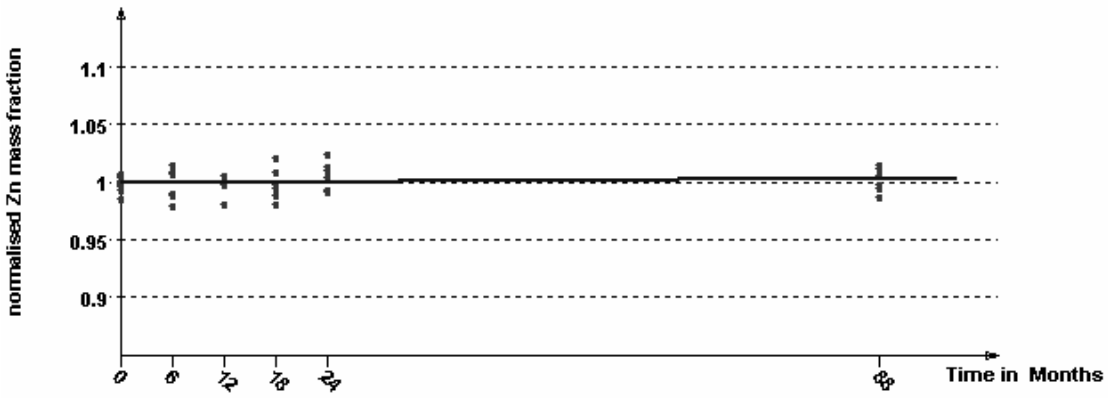


Figure 31: Stability graph for Zn, 18 °C

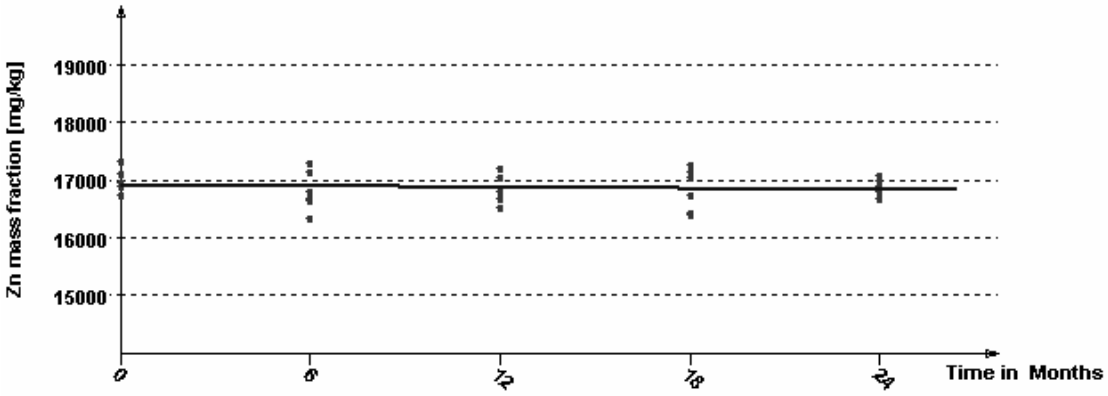


Figure 32: Stability graph for Zn, 40 °C

Annex 4: Data from characterisation studies

Table 17: Individual results for As (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
01	k0-NAA	54.4	52.9	52.2	52.3	51.7	53.5
02	HGAFS	42.5	41.1	41.2	40.2	43.3	43.7
03	ICPAES	56.7	51.4	52.2	56.1	46.1	47.6
03	ICPMS	50.9	52.1	49.0	51.9	54.0	53.4
04	INAA	89.3	89.1	89.4			
05	ICPMS	61.9	60.4	59.4	59.3	62.7	58.9
06	INAA	56.3	56.3	55.3	56.5	56.6	57.0
07	HGAAS	41.9	42.1	40.9	41.3	40.6	42.6
08	INAA	58.3	53.5	54.1	52.3	56.7	50.2
10	k0-NAA	50.2	48.5	49.6	50.4	50.8	50.3

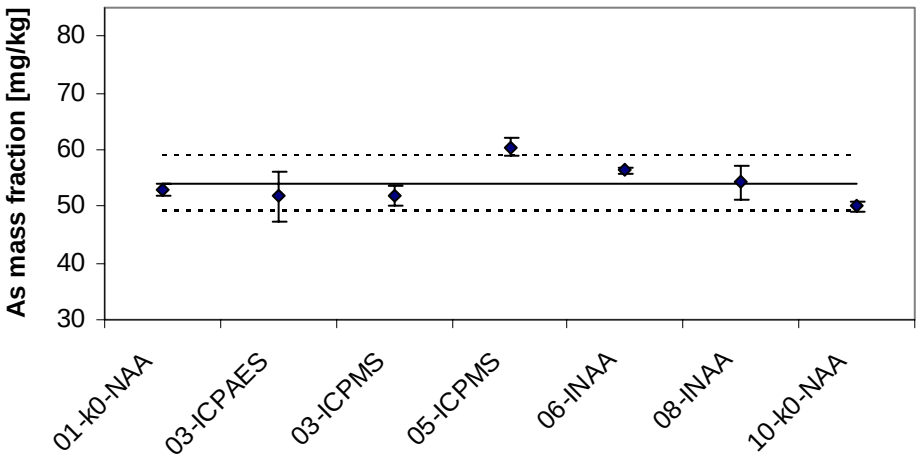


Figure 33: Results for As as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 18: Individual results for Cd (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	ETAAS	225.7	219.1	218.7	231.2	227.2	217.7
01	ICPIDMS	227.9	228.8	228.0	228.3	228.9	229.0
01	k0-NAA	239.5	224.8	230.2	226.0	213.9	220.1
02	IDTIMS	214.6	221.6	221.1	222.0	220.8	219.9
02	RNAA	229.0	238.0	233.0	231.0	232.0	223.0
03	ICPAES	218.0	218.0	196.0	216.0	219.0	227.0
05	ICPAES	211.0	212.0	214.0	218.0	221.0	217.0
06	INAA	246.0	248.8	250.7	249.1	249.3	245.7
07	FAAS	206.0	215.0	213.0	217.0	211.0	215.0
07	ICPMS	210.0	219.0	220.0	220.0	219.0	221.0
11	ICPIDMS	222.4	223.8	223.3	219.7	222.8	220.6

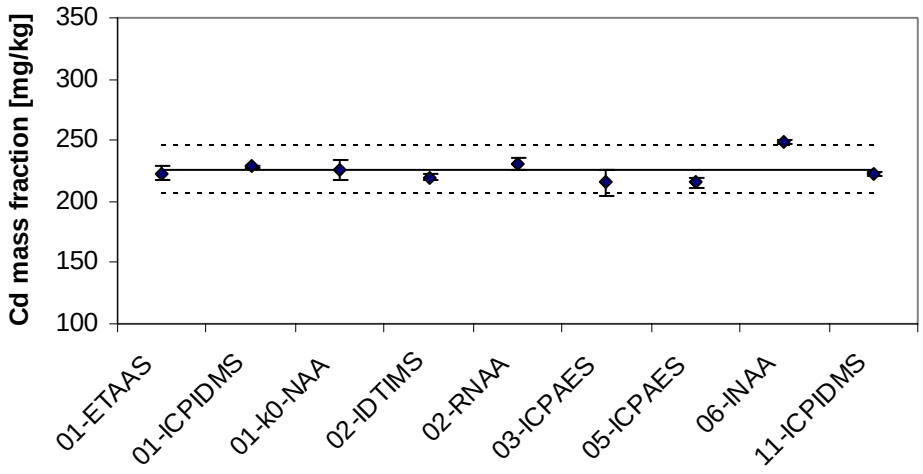


Figure 34: Results for Cd as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 19: Individual results for Co (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
01	ETAAS	22.3	24.5	20.3	24.3	21.4	25.1
01	k0-NAA	27.8	27.1	27.2	27.6	26.7	27.5
03	ICPAES	24.4	25.0	24.2	25.0	24.6	24.1
03	ICPMS	26.1	25.0	24.6	26.4	24.5	24.8
05	ICPMS	27.5	27.7	27.9	28.6	28.3	27.9
06	INAA	27.7	27.9	27.5	27.0	28.0	27.8
07	ICPAES	19.3	12.6	19.3	16.0	19.3	22.7
07	ICPMS	22.6	23.2	23.1	23.1	23.3	23.5
10	k0-NAA	27.4	26.9	27.1	27.3	28.0	27.9

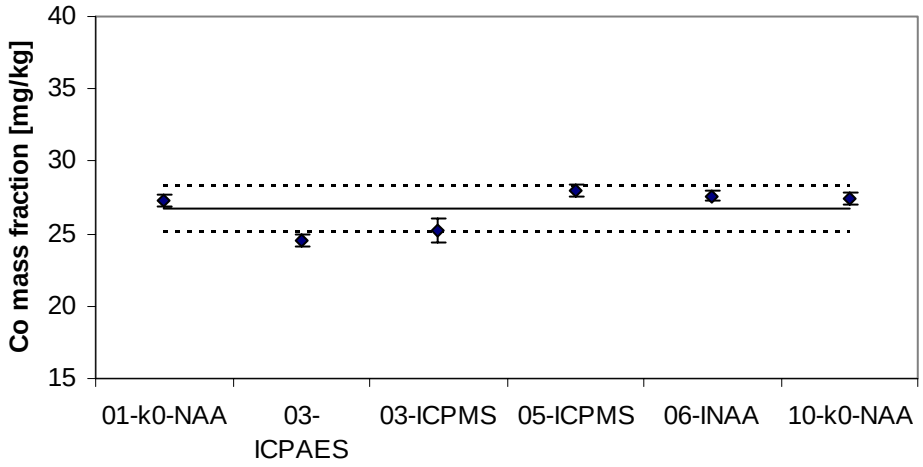


Figure 35: Results for Co as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 20: Individual results for Cr (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	k0-NAA	818.9	802.2	803.5	816.2	799.1	818.1
02	IDTIMS	808.0	819.9	830.5	839.1	815.4	801.3
03	ICPAES	447.0	431.0	428.0	433.0	376.0	421.0
04	ETAAS	784.0	794.0	885.0	805.0	840.0	895.0
04	INAA	887.0	879.0	768.0			
05	ICPAES	751.0	776.0	745.0	758.0	772.0	778.0
06	INAA	770.7	779.3	769.8	781.1	780.2	766.9
07	ICPMS	237.0	248.0	247.0	252.0	251.0	247.0
08	INAA	898.7	858.6	852.8	846.9	848.5	875.9
10	k0-NAA	811.4	792.6	803.4	805.1	821.8	810.7
11	ICPIDMS	800.0	792.0	772.0	790.0	776.0	772.0

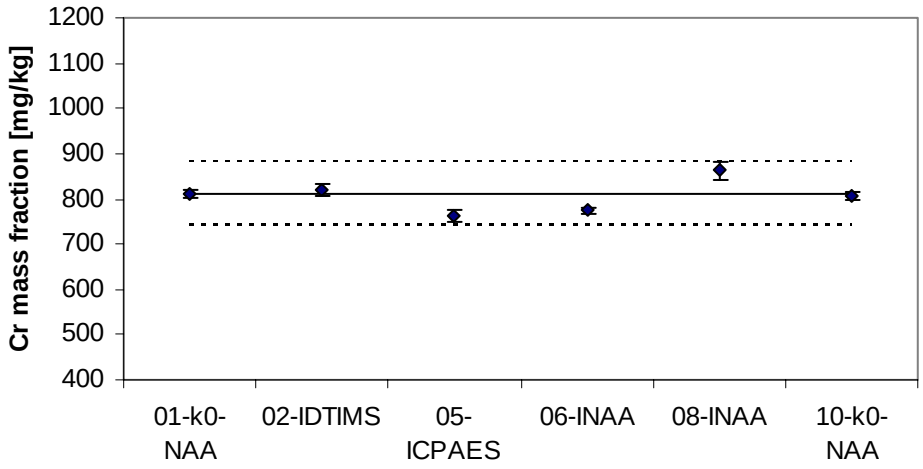


Figure 36: Results for Cr as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 21: Individual results for Cu (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	ETAAS	1072	1100	1080	1056	1037	1094
01	ICPIDMS	1050	1051	1054	1053	1047	1068
02	IDTIMS	1077	1065	1049	1035	1021	1013
03	ICPAES	963	956	939	1011	978	974
05	ICPAES	1081	1072	1071	1075	1070	1068
06	INAA	1103	1015	1028	1000	1047	1098
06	RNAA	1027	1028	1007	1037	1087	1000
07	FAAS	971	1006	1005	1005	1000	999
07	ICPMS	944	950	967	974	961	971
09	ICPIDMS	1055	1060	1058	1095	1088	1104
11	ICPIDMS	1118	1102	1074	1109	1079	1095

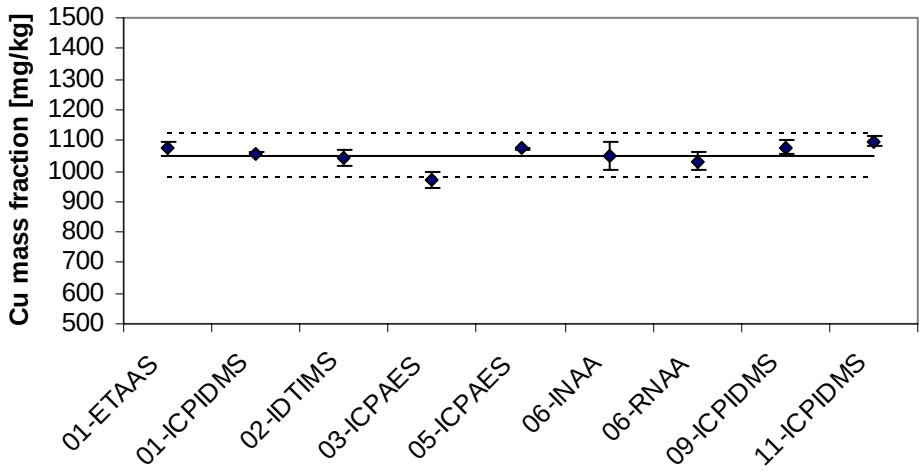


Figure 37: Results for Cu as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 22: Individual results for Fe (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	k0-NAA	13194	13001	13105	12958	12840	13081
02	IDTIMS	13681	13560	13611	13458	13804	13568
03	ICPAES	13470	12210	13610	13390	12960	13020
05	ICPAES	13213	13093	13290	13269	13284	13226
06	INAA	12550	12770	12300	13030	12500	12830
07	FAAS	13600	13400	13100	13000	13200	13100
07	ICPAES	11900	12100	12100	12200	12200	12300
07	ICPMS	13130	13970	12890	12390	10530	11590
10	k0-NAA	12750	12550	12690	12850	13060	12940

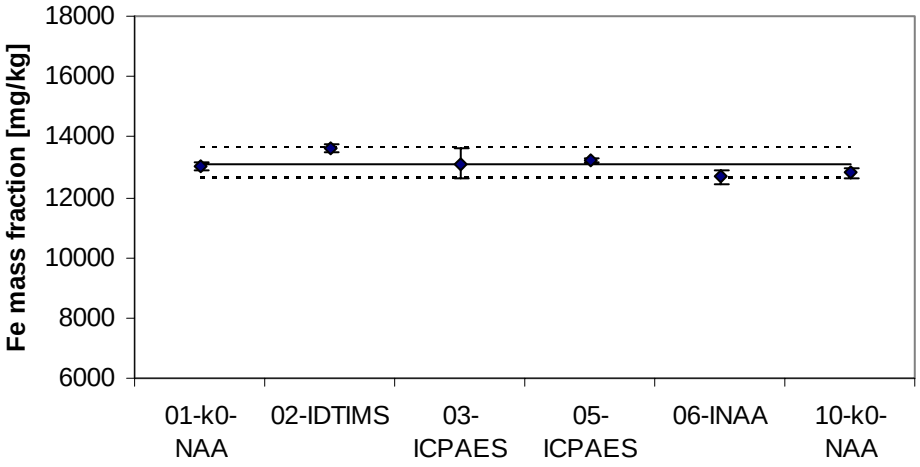


Figure 38: Results for Fe as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 23: Individual results for Hg (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
02	CVAAS	1.39	1.41	1.42	1.36	1.46	1.43
02	RNAA	1.78	1.84	1.69	1.61	1.55	1.68
03	AFS	1.51	1.57	1.48	1.46	1.46	1.57
04	HGAAS	1.30	1.20		1.20	1.50	
04	ICPMS	1.60	2.40		1.90	2.10	
05	CVAAS	1.52	1.48	1.44	1.56	1.52	1.44
07	CVAAS	1.46	1.37	1.45	1.43	1.37	1.37
11	ICPMS	1.99	1.96	1.66	1.87	2.03	1.87

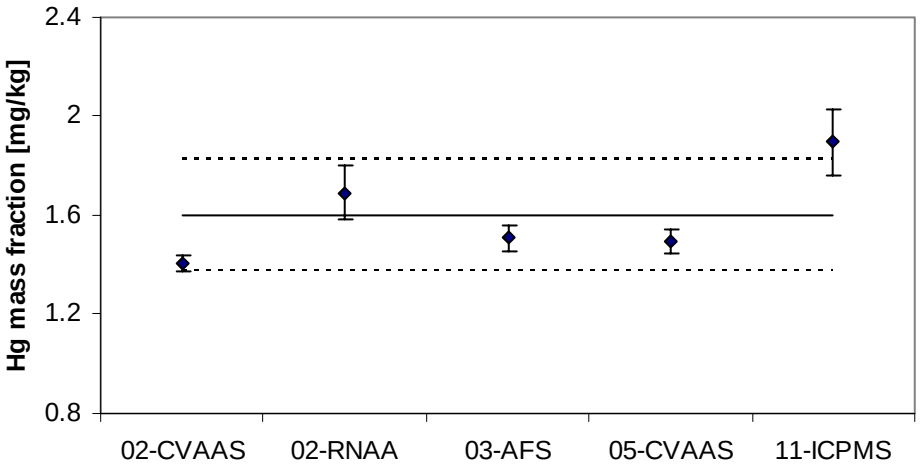


Figure 39: Results for Hg as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 24: Individual results for Mn (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
02	INAA	687.0	693.0	689.0	695.0	683.0	708.0
03	ICPAES	746.0	797.0	747.0	737.0	742.0	728.0
03	ICPMS	724.0	698.0	747.0	717.0	687.0	738.0
04	ETAAS	726.0	772.0	704.0	770.0	699.0	735.0
05	ICPAES	718.0	726.0	722.0	725.0	718.0	723.0
06	INAA	747.3	726.5	778.4	763.3	730.4	750.5
07	FAAS	664.0	696.0	693.0	700.0	690.0	695.0
07	ICPAES	685.0	698.0	693.0	700.0	700.0	704.0
07	ICPMS	679.0	688.0	700.0	700.0	700.0	705.0

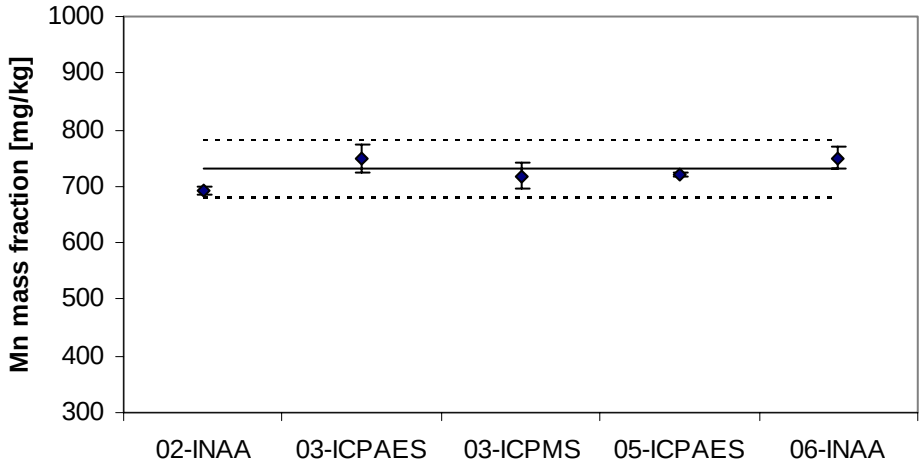


Figure 40: Results for Mn as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 25: Individual results for Ni (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	ETAAS	120.3	114.9	116.3	116.7	119.3	113.3
02	IDTIMS	113.9	116.0	116.8	114.6	120.9	115.0
02	RNAA	135.0	108.0	104.0	95.0	137.0	137.0
03	ICPAES	118.0	114.0	113.0	119.0	115.0	113.0
04	INAA	133.0	109.0	< 300			
05	ICPAES	106.6	105.3	104.8	106.7	114.4	102.0
06	INAA	118.6	123.0	123.0	118.7	124.9	121.0
07	FAAS	82.1	85.4	82.9	85.0	83.6	83.6
07	ICPMS	97.9	101.0	100.0	101.0	101.0	102.0
11	ICPIDMS	122.6	116.6	111.6	118.8	114.5	117.9

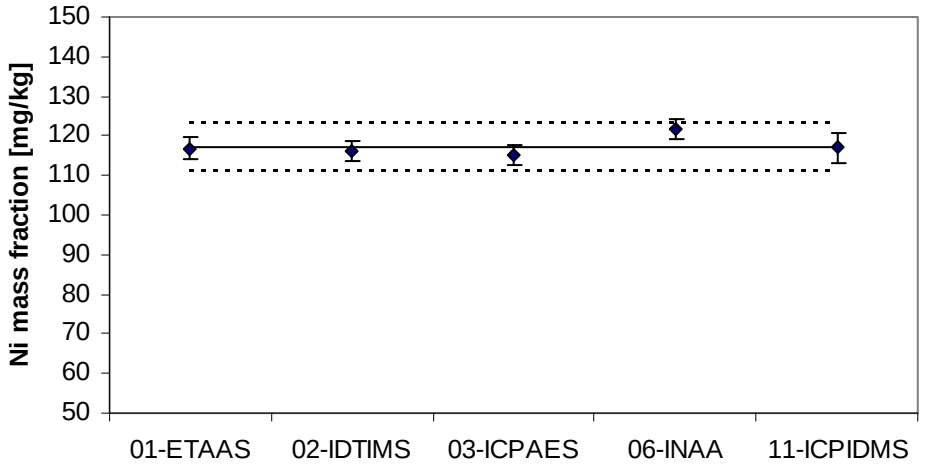


Figure 41: Results for Ni as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 26: Individual results for Pb (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
01	ETAAS	4689	4627	4829	4683	5291	5042
01	ICPIDMS	5060	5090	5020	5010	5050	5050
02	IDTIMS	5166	5163	5184	5157	5159	5121
03	ICPAES	4410	4260	4090	4690	4520	4610
03	ICPMS	4330	4300	4080	4330	4430	4460
05	ICPAES	5048	5005	4948	5094	5041	5056
05	ICPMS	4677	4774	4763	4689	4971	4898
07	FAAS	4707	4878	4849	4872	4802	4832
07	ICPMS	4880	5080	5020	4950	5000	5080
09	ICPIDMS	4987	4981	4959	4881	4801	4842
11	ICPIDMS	4688	4689	4568	4622	4616	4642

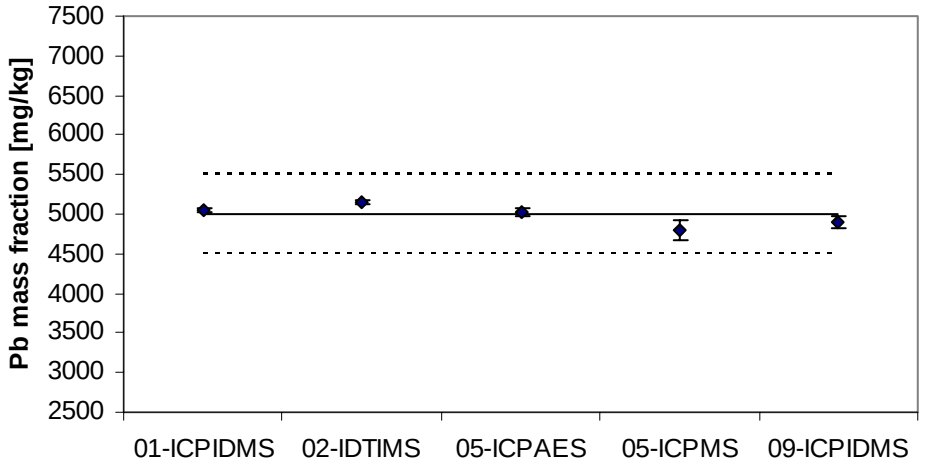


Figure 42: Results for Pb as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 27: Individual results for Sb (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
01	k0-NAA	884.6	870.1	880.3	879.3	865.0	877.8
03	ICPAES	837.0	846.0	845.0	830.0	877.0	855.0
03	ICPMS	824.0	807.0	820.0	833.0	808.0	823.0
04	INAA	1030.0	998.0	969.0			
05	ICPMS	839.0	851.0	855.0	851.0	888.0	824.0
06	INAA	763.3	753.5	737.3	759.1	754.7	765.0
07	HGAAS	532.0	445.0	471.0	395.0	377.0	425.0
08	INAA	994.0	994.8	992.8	970.0	943.0	944.7
10	k0-NAA	846.9	833.9	844.2	848.5	853.1	860.3
11	ICPIDMS	939.0	933.0	927.0	921.0	934.0	914.0

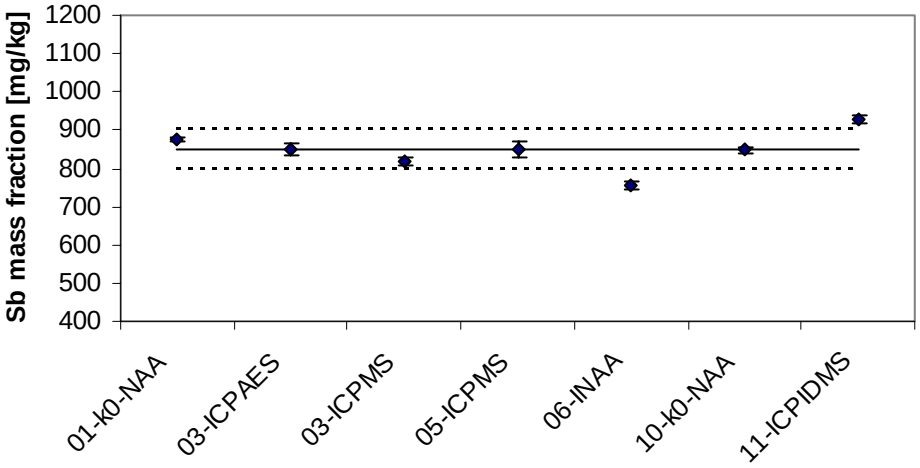


Figure 43: Results for Sb as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 28: Individual results for Se (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
01	k0-NAA	18.4	17.7	18.5	18.1	18.1	20.1
02	RNAA	16.7	14.7	14.5	17.0	17.5	16.3
03	ICPAES	19.2	19.6	18.0	18.9	19.8	17.8
03	ICPMS	20.2	19.1	17.3	18.8	21.1	19.2
04	HGAAS	42.8	43.4	42.0	44.4	41.4	42.6
05	ICPMS	20.1	20.0	19.6	18.1	19.9	
06	INAA	18.3	17.2	18.4	17.8	17.6	18.1
07	HGAAS	13.5	13.4	14.4	14.2	13.1	13.6
07	ICPMS	13.4	14.1	14.8	14.7	14.2	15.0
10	k0-NAA	18.1	18.1	18.0	18.1	18.1	18.2

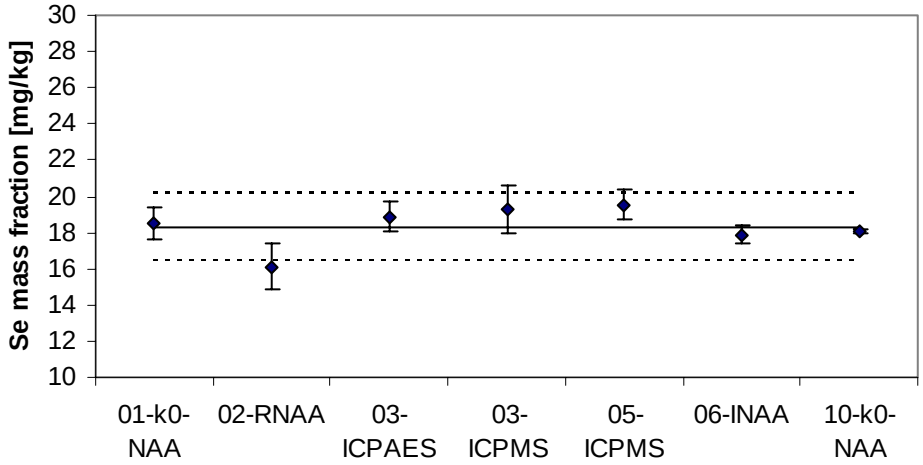


Figure 44: Results for Se as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 29: Individual results for Tl (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
02	IDTIMS	1.33	1.31	1.33	1.32	1.33	1.33
03	ICPMS	1.36	1.31	1.25	1.36	1.35	1.32
05	ICPMS	1.29	1.27	1.25	1.18	1.21	1.20
07	ICPMS	1.13	1.20	1.18	1.21	1.20	1.21
11	ICPIDMS	1.65	1.60	1.65	1.61	1.63	1.62
12	ICPIDMS	1.41	1.42	1.42	1.40	1.41	1.42

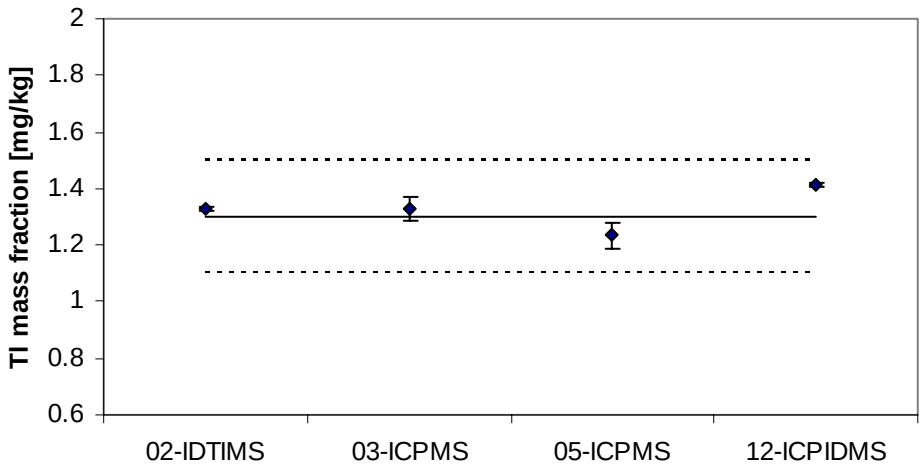


Figure 45: Results for Tl as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (—— : certified value, – – : expanded uncertainty of the certified value)

Table 30: Individual results for V (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background. Results for Lab 03 are presented as individual results, but are only used as one set of data for the evaluation.

Lab no	Method acronym	Individual results					
02	INAA	42.0	38.5	35.6	37.1	41.8	39.8
03	ICPAES	38.5	35.9	37.0	38.7	36.2	37.4
03	ICPMS	31.8	29.9	29.4	33.6	31.3	30.0
04	ETAAS	33.7	31.0	40.1	32.9	36.3	44.4
05	ICPAES	34.1	34.6	37.6	33.9	37.0	36.2
06	INAA	32.7	32.9	34.7	34.1	32.0	32.7
07	ICPAES	19.1	10.4	17.8	12.7	18.8	20.2
07	ICPMS	30.7	31.9	33.4	33.7	34.1	35.7

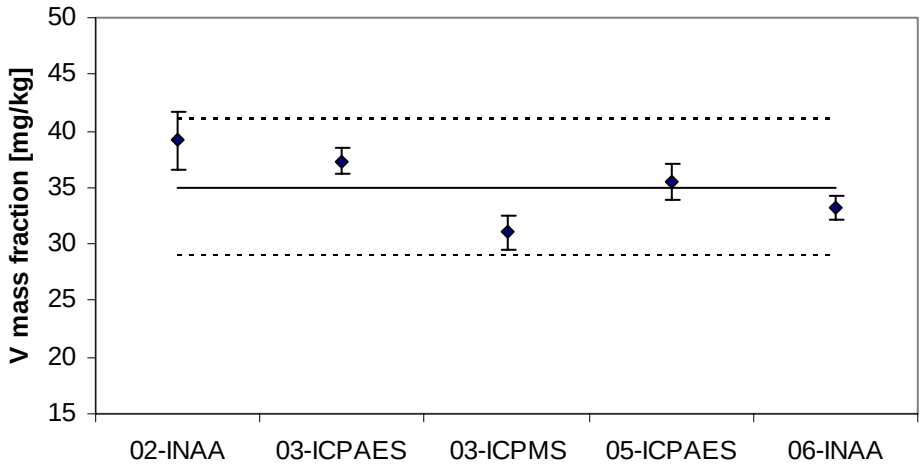


Figure 46: Results for V as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

Table 31: Individual results for Zn (data expressed in mg/kg). Data not included in the final evaluation is indicated by a grey background.

Lab no	Method acronym	Individual results					
01	FAAS	16830	16960	16770	16710	16660	16710
01	k0-NAA	16920	16520	16750	16870	16330	16880
02	IDTIMS	17270	17080	17040	16920	17000	16990
03	ICPAES	17700	16030	17800	17500	16980	16960
05	ICPAES	15710	15860	15900	15590	15830	15780
06	INAA	16730	16520	16800	16600	16780	16640
07	FAAS	15800	16300	16300	16500	16400	16300
07	ICPAES	14700	15000	14900	15000	15100	15100
07	ICPMS	15200	16100	15700	16100	16300	16400
10	k0-NAA	16720	16360	16630	16620	16920	16700

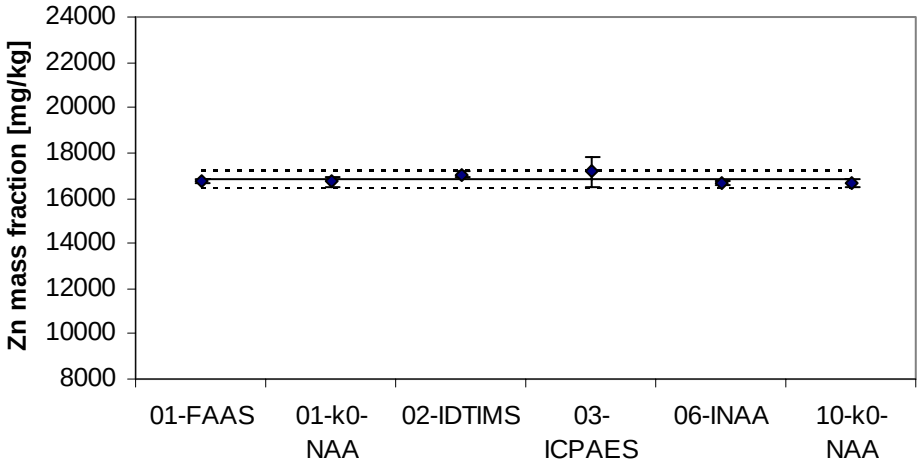


Figure 47: Results for Zn as used for characterisation. Uncertainty bars represent the standard deviation of each lab's results. (── : certified value, – – : expanded uncertainty of the certified value)

European Commission

EUR 22667 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements –
The Certification of the Mass Fractions of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, V and Zn in fly ash, BCR-176R
Authors: A. Held, G. N. Kramer, P. Robouch, U. Wätjen
Luxembourg: Office for Official Publications of the European Communities
2007 – 73 pp. – 21.0 x 29.7 cm
EUR - Scientific and Technical Research series; ISSN 1018-5593
ISBN 978-92-79-04998-9

Abstract

This report describes the preparation and certification of the fly ash Certified Reference Material (CRM) BCR-176R. It replaces its exhausted predecessor, BCR-176. The CRM was processed and certified by the European Commission, Directorate General Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

The CRM was prepared from a fly ash collected in the electrostatic filters of a city waste incineration plant. After milling the resulting powder was filled in glass bottles containing 40 g powder.

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

The new CRM has been certified for its content of As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Se, Tl and Zn .

Indicative values have been established for Hg, Mn and V.

This CRM is intended for use in quality assurance of measurements of heavy metals in fly ash and related matrices

	Mass Fraction	
	Certified value [1] [mg / kg]	Uncertainty [2] [mg / kg]
As	54	5
Cd	226	19
Co	26.7	1.6
Cr	810	70
Cu	1050	70
Fe	13100	500
Ni	117	6
Pb	5000	500
Sb	850	50
Se	18.3	1.9
Tl	1.32	0.21
Zn	16800	400

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified values are traceable to the SI.
2) Expanded uncertainty with a coverage factor k = 2 according to the Guide for the Expression of Uncertainty in Measurement, corresponding to a level of confidence of about 95 %.

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Community. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

15 LA-NA-22667-EN-C

ISBN 978-92-79-04998-9

Publications Office
Publications.eu.int